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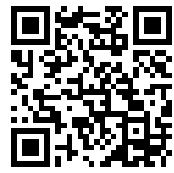

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Transactions of the Faraday Society

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY CHEMICAL PHYSICS, METALLOGRAPHY AND KINDRED SUBJECTS

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VOL. IV. 1908.

London
PUBLISHED BY THE FARADAY SOCIETY,
82, Victoria Street, London, S.W.

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FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. IV. JUNE, 1908. PART 1.

ON CERTAIN ASPECTS OF THE WORK OF LORD KELVIN.

BY SIR OLIVER LODGE, F.R.S.

(*Presidential Address to the Faraday Society, delivered May* 26, 1908, Sir JOSEPH SWAN, F.R.S., PAST PRESIDENT, *in the Chair.*)

When a man of the first magnitude works continually at a single group of subjects from an age preceding twenty to an age exceeding eighty, the circumstance is so exceptional and the output so enormous that no ordinary summary or criticism can do it justice.

It is only therefore with some aspects of that work that I propose to deal; and, unconsciously I suppose, I select those aspects which from one or another point of view have specially impressed myself. I shall, however, except from even these all that portion which relates to practical applications; partly because this portion has been dealt with elsewhere, but chiefly because on this occasion it is appropriate to review those portions of the work which are on the border-land of Chemistry and Physics, or else are where Physics runs into Philosophy—those portions, namely, which would have been specially likely to arouse the interest of our godfather Faraday.

But even here I must make large omissions,—for no particular reason except that, even when they are made, the remainder is more than can be dealt with in any reasonable time.

Among the regions of work omitted altogether are those concerned with the tides, with navigation, with the size of atoms, with the age of the earth, with heat-conduction, with electrostatics and electric images, with elasticity, with physical optics, with static magnetism, and with telegraphy.

I shall not aim at any chronological sequence, and, in fact, propose to begin with those later physico-philosophic views which seemed to determine the direction of his thoughts and the attitude of his mind to nascent and contemporary discoveries in recent years.

For this aspect, even if difficult to treat of, is one which a biographer is bound in some fashion or another not to shirk; and, although myself unable to regard it with full sympathy, I am confident that my point of view is neither presumptuous nor disrespectful.

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Kinetic Theory of Solidity.

Now, I confess that for some years before his death Lord Kelvin's attitude to fundamental physical or philosophical questions was somewhat of a puzzle to me. He seemed to be abandoning ground which he himself had opened up to explorers, and discouraging others from advancing in directions where he himself had pioneered. As a matter of fact, I was uncertain whether his position was even consistent and logically tenable or not; and at the British Association meeting at Leicester, during a discussion on the constitution of the atom in Section A, I had an opportunity of respectfully and deferentially challenging him on this subject. He responded, as always, in the kindest manner, and with great and almost exceptional lucidity indicated what had now become his position. I would not be understood as implying that he carried conviction, or led me to regard that position as a desirable one to occupy; but he showed it to be a consistent and logical one, which he had every right to occupy if he chose, and on which therefore it must be left for posterity, or at least for effluxion of time and progress of discovery, to pass anything in the nature of ultimate judgment.

I was much interested in this pronouncement, and before leaving Leicester jotted down a few notes concerning it, with a view to publishing them in his lifetime, in order that he might, if he chose, add to, or subtract from, or modify the statement. Other things prevented rapid publication, however, and accordingly it is too late for one of the objects in view, but still the notes are worth publication as suggesting genuine antithetical or alternative views of the universe. Accordingly they will appear in a forthcoming number of *Nature*.

It may seem as if the real antithesis was between the postulates of a connecting medium, on the one hand, and of action at a distance across empty space, on the other, and as if Lord Kelvin were in favour of the latter view. I do not, however, think it would be fair to attach to him that responsibility. I think it was more a matter of practical politics with him than a philosophical conception. I think he would have liked to see an explanation in terms of a connecting medium if it could have been managed; but, after spending some years in the attempt, he abandoned it either as too difficult or as hopeless, and constrained himself to be satisfied with unexplained forces between masses of matter acting according to specified laws; the question of the medium or mechanism through which they acted being left out of account as unnecessary from the point of view of practical dynamical calculation and consistent reasoning.

He did speak at times, however, as if immediate action across empty space would be logically satisfactory to him, and quite good enough as an explanation,—the only question being, was it the true one? To me I confess that any such philosophic scheme must necessarily be a cold and merely descriptive account of material activity—that it must necessarily fail to go to the heart of the matter or to constitute what may more reasonably be called "explanation." The conception of forces acting according to a specified law of distance is capable of yielding dynamical results truly, but not of explaining them. Explanation, however, is never ultimate; so it may be that the process contemplated, and in his last years energetically worked at, by Lord Kelvin is an intermediate stepping-stone, which must be taken in order to cross to some more stable resting-place beyond; just as has happened in the case of gravitation.

The above is an attempt fairly to represent what I conceive must have been in the mind of our great leader, and it was a kind of pronouncement

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which I hoped to draw from him by the publication above mentioned. If he had been living it would have been presumptuous to try and state more concerning his views than he himself had indicated; and still it is to be hoped that any one acquainted with his mind on this matter will make the necessary corrections.

Energy.

If we now proceed to ask what great generalisation will for ever be associated with Lord Kelvin's name, and in future ages stand out as his greatest achievement, it is not easy amid the wealth of material to focus it clearly. A few days ago I myself should not have been certain, if suddenly catechised, what my answer would be to such a question. But in preparing this address, and reading once more some of his early Papers, I find nothing greater than what emanated from him in and about the year 1851, when he was immersed in the doctrine of energy. I do not mean, of course, any single year exactly, but about that period of his life; for in the records of that time are to be found, I think, his greatest and strongest memoirs.

The keenness and penetration of his mind at that epoch must have been something astounding. With all his mathematical powers alert, with tremendous natural genius, and extraordinarily vivid interest in phenomena of all kinds, he seized the facts concerning energy as they emanated from Carnot and from Joule, and with them in his mind, more powerfully and persistently than even Helmholtz, he brooded over the whole domain of physics till he elicited therefrom a series of the most beautiful and striking discoveries,—discoveries, which as they have gained in familiarity, have perhaps lost something in charm, by constant iteration in textbooks and college lectures, but which in their freshness well repay an attentive perusal; though their form is far inferior to their substance.

So I expect that the answer of posterity to the question above mooted will be that his most immortal work is the development and application of the doctrine of the Conservation of Energy, together with the comprehension and elaboration of the laws of Thermo-dynamics.

Later he became more immersed in the work of the world, managed a great deal of practical business, and made many inventions of surpassing ingenuity; but although all this later work is the best known to the general public—if indeed any scientific work can be said to be really known to that body—yet in pure genius nothing to my mind, since Newton, comes up to his achievement in the fifth and sixth decades of the last century, especially from 1848 to 1856.

The comprehensive recognition, and extraordinary application to physics, of Carnot's brilliant "Reflexions on the Motive Power of Fire," or as we should now say *On the efficiency of heat engines*, must have been largely due to Lord Kelvin's influence, and to the clear and enthusiastic way in which he took up and developed the subject. It is singular that this discovery of the second law of thermo-dynamics, which came historically first, created a real difficulty and obstruction in the recognition of the truth of what is now called the first law; and Joule's work would not only have been rejected by the Royal Society, as it was, but would have met with a total lack of recognition, or even disdain, had it not been for Lord Kelvin's perception of its value at a meeting of Section A of the British Association in 1847. In fact, the development of the whole subject of thermo-dynamics, though extensively carried out by Clausius and others, must have received strong initiative from him.

But it was not the mere recognition of the true nature of heat as a form of

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energy—so that when work was done by a fall of temperature the heat removed was less than the heat supplied, thereby breaking down the hydraulic analogy—but it was the way in which, both by Lord Kelvin and Helmholtz, the conservation of energy was applied all over the ground of physics, and especially so as to incorporate electrical phenomena with the rest, in one scheme, that was most remarkable.

Of all the memoirs dealing with the conservation of energy as applied to electricity, perhaps the most striking, though one of the simplest, is Lord Kelvin's early paper on Transient Currents, or the discharge of an electric capacity; wherein he gives the whole theory of electric oscillations, in so far as they can be treated without recognising the radiation which accompanies them—a discovery reserved for Maxwell.

The three quantities to be expressed are: the kinetic energy of the current itself, the rate of production of heat as investigated by Joule, and the energy corresponding to the storage of charge in a condenser—that is to say, the term $\frac{1}{2}SV^2$, or $\frac{1}{2}\frac{Q^2}{S}$. Any change in this energy, due to current $\left(C=-\frac{dQ}{dt}\right)$, must be accounted for by frictional generation of heat and by inertia acceleration. The energy of the latter term was essentially discovered by Lord Kelvin in this Paper (*Phil. Mag.*, Jan., 1853) as an outcome of previous papers in 1851 and 1848 (Arts. xxxv. and liv. of Vol. I. of *Math. and Phys. Papers*). These contain the first statement, so far as I know, of the kinetic energy of a current. He wrote it as $\frac{1}{2}AC^2$, and called A "the electro-dynamic capacity of the discharger." This coefficient A was a most puzzling quantity at the time, and indeed was rejected by many so-called practical electricians, for long afterwards, though it is what we now familiarly speak of and measure as self-inductance. Difficulties felt by Lord Kelvin himself, before introducing it, are indicated on page 490, Vol. I. The whole theory of electric oscillations follows from the energy equation (page 543)—

$$d\left(\tfrac{1}{2}\frac{Q^2}{S}\right) = RC^2dt + d\left(\tfrac{1}{2}LC^2\right),$$

or, writing x for Q, simply—

$$L\ddot{x} + R\dot{x} + \frac{x}{S} = 0;$$

which, though now we write it glibly enough, was a considerable inspiration in 1853, more than half a century ago; though the difficulties can hardly be appreciated without a study of the paper and of those which precede it.

The extraordinary magnitude of the giants in physical science, especially in mathematical physics, during the Victorian era, and indeed throughout the nineteenth century, will probably be recognised more fully by posterity than by us. It will be many generations, probably many centuries, before the general and literary world can receive any adequate impression on the subject, or begin to understand their methods and their more recondite results.

Conservation of Energy Applied to Electricity.

A mode in which I have been accustomed to state to students the law of conservation as applied to current electricity, gradually introducing its several terms and thereby covering almost the whole area of the sub-

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ject, so far as fundamentals are concerned, may perhaps be briefly indicated.

Current is defined as $C = \frac{dQ}{dt}$; and the work done when a quantity dQ is transferred down a step of potential is $(V - V')\,dQ$, or, as it may otherwise be written, $EC\,dt$. That is the energy to be accounted for, and represents the left-hand side of the equation. On the right-hand side we have, as the necessary first term, the frictional generation of heat; and the fact that the opposing force is accurately proportional to the first power of the current (which is Ohm's law), gives us as heat energy $RC\,dQ$, or, as it is commonly written, $RC^2\,dt$; though of course, strictly speaking, the *square* of a current, just like the square of a time, is really nonsense. All such expressions correspond merely to a convenient grouping of quantities which in common sense and reality are otherwise grouped.

Parenthetically also the R, which was originally denominated by Kelvin "the galvanic resistance of the discharger," and commonly called resistance, is really only a *resistance coefficient;* it is the factor by which to multiply the current in order to give the frictional or irreversible opposition E.M.F.

So far the equation runs, simply, $EC\,dt = RC^2\,dt$; and Ohm's law is an assertion that, at constant temperature, R is constant—*i.e.*, is not a function of current.

The next term that may be attended to is the inertia term, depending on electric acceleration—a term which is zero so long as the current is steady or obeying the first law of motion, but which is of great importance whenever the current strength, and therefore the magnetic field enclosed by it, varies. If by any means the number of effective lines of force encircled by the current is increased by dN, the corresponding increase of energy is $C\,dN$, and this therefore is the next term, and represents the energy of magnetic induction. So the equation now is $EC\,dt = RC^2\,dt + C\,dN$, and yields at once the fundamental dynamo and motor equation—

$$\frac{dN}{dt} = E - RC = \text{generated or back E.M.F.}$$

But as it stands the term $C\,dN$ is very comprehensive, and may be separated out into self-induction, mutual induction, and induction by outside magnets:—

In self-induction the N is proportional to the current; it is equal to current multiplied by an appropriate coefficient L, dependent on the geometry of the circuit and on the material inside it. The self-induction term may therefore be written $LC\,dC$; though there are cases, as in a commutated armature, when the L varies too, in which case we shall have an additional term $C^2\,dL$, and dL/dt will be a spurious or apparent resistance.

For mutual induction the corresponding energy term will be $C\,d(MC')$.

For any number of magnetic poles the energy will be $C\,d(m\omega)$, where ω is the solid angle which the circuit subtends from each.

All these and other varieties are special cases of the term $C\,dN$.

So the equation becomes, in one important and most simple case—the case of any circuit whatever in which the current is not necessarily steady or is not yet fully established—

$$EC\,dt = RC^2\,dt + LC\,dC.$$

When there is no battery $L\frac{dC}{dt} + RC = 0$, or, if there is a discharging condenser in the circuit, $= \frac{1}{S}\int_t^o C\,dt$.

Now we come to a peculiarly Kelvin term, when the current decomposes

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a liquid, giving rise to a quantity of decomposed material, the thermal value of whose reaction per gramme is θ. Accordingly we shall have as the next energy term $\Sigma(J \cdot \theta dm) = \Sigma(J\epsilon\theta)\, dQ = \Sigma(J\epsilon\theta) C dt$, where ϵ, or dm/dQ, is the electrochemical equivalent of the substance; giving the well-known expression for polarisation E.M.F., $J\epsilon\theta$, which dates actually from 1851.

Next there is the possible passage of a current across the junction of two materials to be considered; for *there* must exist the contact force which is responsible for the Peltier effect. It is true that Lord Kelvin identified this with a mere temperature-variation of the so-called Volta contact-force, whereas I regard that as not so much physical as chemical, and represented by the previous term instead of by this thermo-electric term. But undoubtedly there is a contact force at the junction of two metals, and immensely more at the junction of a metal and an insulator; though I do not suppose that any metal-metal force has the value which he was inclined to attach to it. If the temperature is uniform, the forces balance; but if not, we must add an energy term, $\Sigma(\Pi) dQ$.

Next comes the E.M.F. caused by the passage of a current along a slope of temperature—a phenomenon discovered by Lord Kelvin himself, first theoretically and then experimentally, and expressed by him as exhibiting a curious analogy with specific heat. The term for a simple circuit of two metals, with junctions at temperatures T_1 and T_2, may be written $dQ\int_1^2(\sigma_a - \sigma_b)\, dT$, where each σ is the Thomsonian specific heat-capacity of electricity in a substance.

The result deducible from all this is that a current generated by any E.M.F. E, applied to a circuit, is in general opposed, first by the inevitable frictional or ohmic resistance, and next by a number of possible opposition or polarisation forces which can be enumerated as follows:—

(1) a self-induced back-E.M.F. which vanishes when the current is steady;

(2) a magnetically-induced E.M.F., due to moving or varying magnets, or to reaction from other electric circuits;

(3) a chemical polarisation force proper, at electrodes in liquids;

(4) a Peltier force at every junction of two conductors;

(5) a Thomson force, in all conductors with a gradient of temperature;

(6) and the current is also opposed by reaction from any mechanical work done, as by an electric motor or any other contrivance developing energy W of any kind.

This is all quantitatively expressed by cancelling dQ from the energy equation above built up, and writing it thus:—

$$E = RC + LdC/dt + dN/dt + \Sigma(J\epsilon\theta) + \Sigma(J\Pi) + \Sigma\int J\sigma dT + dW/dQ.$$

Specific Heat of Electricity and Volta Force.

It seems to me an amazing piece of insight which led Lord Kelvin at that date, 1851, to attribute to electricity, even hypothetically and only for convenience, something akin to real specific heat. The fact was really discovered in 1851, though he did not verify it experimentally till 1856 (see pages 246 and 319, &c., of that monument of human power, Vol. I. of *Math. and Phys. Papers*). The modern theory of electrons—which are now supposed to be flowing in great crowds through a conducting metal, and which by their irregular motions must account for some of the heat energy of a substance, in addition to the much larger portion corresponding to the motion of the atoms—seems to justify this curious expression, "specific

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heat of electricity," to an unexpected degree; and thermo-electric phenomena may be stated in terms of a definite pressure of these mobile and detached electrons in any given substance, after the fashion of the pressure of a gas or the osmotic pressure of a salt dissolved in a liquid.

There is, indeed, no obvious reason for denying that the Volta force might be expressed in this way too, were it not that a perfectly valid *vera causa* for this effect is to be found at the surface of the metals, where they are in contact with air or other chemically potential material; and that the magnitude of the effect, so calculated, from electrochemical and thermal data, agrees with observation in absolute as well as in relative value. These and other facts lead me to maintain that Volta force is an incipient display of potential but not actual chemical activity, at the bounding surface of a metal and a dielectric; but I ought to say that Lord Kelvin differed from this view in 1884, and that he still might not agree with all that is implied in this summary statement.

Thermo-Electricity and Gas Theory.

The splendid way in which the second law of thermo-dynamics was applied to the phenomena of thermo-electricity, so as to establish the laws of a thermo-electric circuit, is too well known to demand notice here. The chief features of it are to be found on p. 249 of Lord Kelvin's *Math. and Phys. Papers*, vol. i.; but the enterprise was, I think, to some extent attended by good fortune, such as often rewards those who do not hesitate to risk something in the development of a theory, leaving it to be corrected, if necessary, by the future. (J. R. Mayer's theoretical estimate of J is another illustration.) It so happens that the thermo-electric theory has demanded very little correction, in spite of the intrinsic uncertainty attending application of the second law to an operation which had one irreversible feature about it—which might have been more relevant than it turns out to be—viz., heat conduction.

As an example of the opposite tendency, however, in Lord Kelvin's mind—for it was a mind which at times was extremely cautious—I think I may instance the difficulty he felt about the Boltzmann-Maxwell theory of the distribution of molecular energy. He always seemed to be troubled with a persistent difficulty about the innumerable degrees of freedom possessed by a molecule, and was unwilling to accept the position that many of these degrees of freedom were out of the running, so to speak—were beside the mark, for the purposes of gaseous theory, inasmuch as it was only those which affected, and were affected by, *collisions* that really mattered. Anything like organised motion, such as that of the planets, is out of the running, of course; and so is any internal motion of the parts of an atom which collisions do not produce or lessen or in any way affect.

It may be said that some collisions, like those which result in chemical combinations, do shake the parts of an atom—as is known by the emission of light. That is quite true, but then these collisions are exceptional; and, moreover, energy so transferred is speedily radiated away. The Boltzmann-Maxwell theory only applies to that which remains a permanently constituent portion of the heat energy of the substance,—that is to say, the energy effective in producing pressure and the other manifestations of temperature,—the unorganised random collision energy; it is this alone which need ultimately distribute itself equally among the parameters, through the agency of innumerable encounters. It is probable,

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however, that Lord Kelvin would not concur in the simplicity of this statement: he continued to be impressed by outstanding difficulties.

Dissipation of Energy.

Of Lord Kelvin's work in connection with the dissipation of energy I shall not say much. I fancy that he himself, and certainly some of his disciples, have been at times inclined to attribute to the law of degradation more ultimate and cosmic importance than properly belongs to it. Its significance is limited to the validity of the terms "heat" and "temperature," and if for any reason those terms cease to have a practical meaning, then the dissipation of energy also ceases to be inevitable. The theory, as originally stated by its author, was formulated as an axiom beginning, "It is impossible by means of inanimate material agency," &c., which at once conveys a suggestion that by some other means it may be possible. The different availabilities of energy of various kinds must be essentially a human and temporary conception, useful and convenient for practical purposes, but not ultimate or cosmic. What devices there are for thrusting aside the inevitableness of dissipation, and so evading the goal of ultimate stagnation, I do not know; they have not yet been discovered by us; but there is nothing inconceivable about them. Maxwell's "demons" is one attempt in that direction; nitrifying bacteria have been suggested as another. It is not at all certain what the influence of "life" may be; and all these agencies have to be eliminated if the uncompromising dissipation of energy doctrine is to be accepted. It was not originally stated in quite uncompromising form (see page 514 of Vol. I.).

The *conservation* of energy is a very different thing: that applies to every form, and is a comprehensive law; but the dissipation of energy has no meaning under circumstances when "heat" and "temperature" are obsolete terms—that is to say, when what we now consider to be unorganised and intractable molecular motions can be dealt with in an individual and organised way. Ultimately and absolutely no operation need be irreversible. Irreversibility means only that things have got temporarily beyond our control, as a fire does sometimes.

Absolute Measurement.

To Lord Kelvin, more than to any one else, we owe the realisation of the system of absolute measurement applied to such intractable quantities as are found in electricity and magnetism. And if the world decides to call its commercial electrical energy unit—now commonly spoken of, in insular fashion, as a Board of Trade Unit, or B.T.U.—by the universally known and appreciated name of "a Kelvin," such a procedure will be entirely appropriate.

Counting, or the enumeration of discrete quantities, is a very easy and natural operation; but Measurement, in the sense of expressing the warmth of a day, or the brightness of a light, or the strength of a current, or the field of a magnet, or the resistance of a wire, or the transparency of a window, or the elasticity of a metal, or the conducting power of a gas, in numerical fashion, is not by any means a simple thing; it usually needs great ingenuity, and sometimes can hardly be done.

The invention of suitable units, and the mode of expressing currents and electromotive forces and resistances in such units, is very far from being an obvious notion; and even now the full meaning of the idea of absolute

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measurement is not in all quarters quite clear. In the first instance it was not always quite clear, I venture to say, even in the mind of Lord Kelvin himself; and a certain partial incompleteness was almost necessary in order to reduce electric and magnetic quantities to simple mechanics. For, as a matter of fact, they cannot be reduced to simple mechanics, or at least have not yet been so reduced; and it was by partially blinding ourselves to that fact that the ideas of the ohm, the ampere, and the volt were attained. We used to be told that resistance was a velocity, and that electrostatic capacity was a length, also that self-induction was a length, and so on. But of course, resistance is not a velocity, nor is self-induction or capacity a length. Nevertheless, had it not been for this partially erroneous simplification, the introduction of any system of electric measurement would probably have been seriously delayed. Incidentally it may be noted that the magnetic method of measuring resistance, or "determining the ohm," was devised by Weber. Kelvin's first method was based upon Joule's law (see page 502, Vol. I.).

Then, again, many people seem to think that absolute measurement has necessarily something to do with the metric system, and with the expression of quantities in the undoubtedly convenient c.g.s. units. On the other hand it has been urged by others that nothing expressed in arbitrary and perishable units, like centimetres, grammes, and the like, could be really absolute; but that a unit independent of convention and humanity and terrestrial considerations, one really eternal and the same throughout the universe, ought to be employed,—such, for instance, as the wave-length of a specified kind of light as the unit of length, the mass of a certain kind of atom as the unit of mass, and the period of some fundamental movement as the unit of time.

Undoubtedly the determination of any conventional unit in terms of these natural units has a distinct value; inasmuch as it enables the conventional unit to be reproduced or understood at any epoch in the world's history, or on any other planet. But it has nothing to do with the principle of absolute measure; nor is it necessary to employ these universal units for practical purposes. The connection between them and the conventional unit is a matter of careful determination, to be performed from time to time; and it is usually expressed in a phrase such as "measurement of the wave-length of light in metres," or "determination of the mass of an atom in grammes," rather than by the converse mode of expression, which to some would seem more appropriate. The fact is, however, that anything will do for a unit of absolute measure, so long as it is definite and constant,—a foot or a yard, is as good as anything else—and it is a great pity that the inventors of the metric system did not employ one of these old historical units instead of a brand new one supposed to be connected with the size of the earth—a comparatively unimportant and irrelevant magnitude. They could hardly have realised that the relation between any two units arbitrarily chosen must necessarily be incommensurable, and that historical continuity was far more valuable than approximate round numbers for relations not frequently wanted. Perhaps they did not realise, either, that old units based on the dimensions of the human body were psychologically sound.

The real essence of absolute measure is that every quantity shall be thoroughly and completely specified, so as to be of the right dimensions without any factor being omitted or understood. Thus, for instance, a foot-pound is not an absolute unit of work, unless the intensity of gravity be included as a factor; nor can a self-induction be expressed as so many earth-quadrants, without the introduction of the factor μ. More than this. Any equation which is only true when the quantities are interpreted in a certain way—as, for instance, if length is expressed in metres, weight in tons, and the like—as

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is done in so many engineering equations—avoids all the advantages of absolute measure : these expressions are not really equations at all, but arithmetical dodges or shorthand statements for immediately practical convenience. For such purposes they are often useful, though their constant employment tends to stunt the theoretical faculties, and seems to hinder perception of the advantages of the more important kind of equation, which, being in absolute measure, is true in every system of units whatever,—an equation in which the symbols represent the quantities themselves, and not some mere numerical relation in terms of a conventional unit.

Take a very simple example. If from a point at a height h above a sphere of radius r a tangent be drawn to the sphere, of length b, then it is absolutely true to say that $h\,(2r + h) = b^2$ (for this is Euc. iii., 36); and this equation, applied to the Earth, gives the distance of the horizon in terms of the height of an observer above the sea. But for immediately practical use it would be convenient to throw it into some arithmetical form, such as this: $1\frac{1}{4}$ times the square root of the height, in feet, will give the distance of the horizon, in miles.

Similarly, the velocity of free fall under gravity, in feet per second, is eight times the square root of the height, in feet; and the *time* of fall is a quarter of the same square root.

These are all handy conventional rules, available for Englishmen; whereas the fundamental equations on which they are based are true in every system of units, and true not only all over the world, but, when properly interpreted, throughout the universe. The interpretation of special cases, in handy form for practical purposes, is entirely legitimate and useful; objection can only be raised when people urge that there is no other kind of equation. In these arithmetical contrivances units must be carefully expressed and adhered to. In every kind of absolute equation it is unnecessary to specify units at all: such an equation expresses a relation between the quantities themselves, irrespective of every arbitrary system of measurement.

Absolute Temperature.

One of the remarkable achievements of Lord Kelvin has been the conception and determination of absolute temperature. The idea of an absolute temperature—that is to say, of a temperature reckoned from a real and actual zero, not a conventional one, and specified so as to be independent of the properties of any particular substance—follows rather naturally from the second law of thermo-dynamics, and from the fact that the efficiency of a perfect or reversible heat engine is independent of the properties of the working substance,—being dependent only on the temperatures at which heat is supplied and withdrawn. Absolute temperature is, in fact, the reciprocal of Carnot's function, as Kelvin showed in 1848 (p. 100, Vol. I., *Math. and Phys.*). And the absolute zero is the temperature at which the working substance has exhausted all its heat in doing work, so that there is none to yield up as waste,—the temperature, in fact, at which a condenser or "cold body" becomes unnecessary.

On a thermal diagram a *scale* of temperature can easily be drawn, as the rungs of a ladder between two adiabatic lines, such that the area of each space is the same. And in order to find the number of rungs, with a given-sized degree, it becomes a matter of experiment to determine the total heat obtainable from an isothermal operation performed on the substance to which the adiabatic lines belong. The measurement necessary can be made

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upon any substance—steam or anything else—but it must be dependent on an actual operation (say an expansion)—not a closed cycle of operations—and on a measurement of the change of energy therefrom resulting.

Lord Kelvin gives as the general expression for the absolute temperature of any substance whatever, whose internal energy is E,—

$$T = \left(p + \frac{dE}{dv}\right)\frac{dT}{dp} - \frac{dE}{dp}\cdot\frac{dT}{dv} \quad \ldots\ldots \text{(A).*}$$

For an ordinary gas $\frac{dE}{dv} = K + c\frac{dT}{dv}$, where K is Laplace's cohesion constant; and $\frac{dE}{dp} = c\frac{dT}{dp}$; so this expression (A) agrees with what we obtain below as equation (5).

The actual determination, as hitherto experimentally made, of the zero of absolute temperature, below which it will be for ever impossible to cool bodies —since at that temperature they possess no heat, and therefore cannot have any more removed—may be said to depend (not necessarily or theoretically but actually as the simplest method in practice), on the conception of a perfect gas in the first place—that is, one whose molecules act upon each other and upon the surrounding walls solely by bombardment, there being no cohesion whatever between the molecules. The temperature at which the pressure of such a gas becomes zero must be simply the temperature of absolute molecular rest, and therefore will be the absolute zero. From the properties of such a gas its absolute temperature could at once be experimentally determined, if only such a gas were actually available for experiment, for it would come out as the reciprocal of its coefficient of expansion. But as a perfect gas is not available, an imperfect gas has to be employed, and a correction made for the amount of its imperfection; the amount of this correction being deduced by reasoning based on its behaviour when subjected to an irreversible operation. For instance, it may be allowed suddenly to expand adiabatically in such a way as to do no external work, and therefore not to cool itself if it were perfect, provided time is allowed for all eddies and streaming motions to subside, and we may then observe the actual consumption of heat or fall of temperature really produced—which would be proportional to the cohesion multiplied by the change of volume. The change of temperature so observed is the chief term in a correction to be applied to the reciprocal of the observed coefficient-of-expansion-under-constant-volume of the imperfect gas.

The experiment as first made by Gay Lussac (Sept., 1806), and later independently and more exactly by Joule, of allowing a gas to double its volume inside a closed vessel, by opening a connection between a full and an empty portion of a vessel, was manifestly an interesting and suggestive experiment, and a check or verification of Mayer's hypothesis that the mechanical equivalent of heat could be obtained by equating the heat supplied and the work extracted from expanding air; but the full meaning and bearing of such an experiment is by no means obvious, and it is remarkable that it should lead to a determination of the zero of absolute temperature. For this purpose it has to be repeated in a more refined form—the oozing of gas as a steady stream from high pressure to low through a porous plug—and a determination made of the change of temperature resulting, when all eddies and organised

* See *Encyclopædia Britannica*, article "Heat."

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kinds of motion have subsided, and when everything has become heat again, except what was lost in internal work.

It is well known now that the practical liquefaction of gases depends on this very effect, for of course without some cohesion between the molecules liquefaction would be quite impossible. The essence of liquefaction is the automatic subdivision of the contents of a vessel into two sharply bounded regions of different density, and the retaining of them in this condition for a time by internal molecular forces.

The elementary argument about the notion of absolute temperature in terms of a perfect gas can be put thus:—

A perfect gas is one whose molecules act on each other, and on the walls of the containing vessel, solely by bombardment. Simple mechanics shows that such a substance exerts a pressure—

$$p = \frac{1}{3}\rho u^2; \quad \ldots \ldots \ldots \quad (1)$$

and whenever it expands all the work done is against external pressure.

The heat in such a body is solely the energy of its irregular or unorganised molecular motion—including rotation as well as translation; and the temperature of such a body can be defined as simply proportional to the heat, or equal to the heat divided by a capacity-constant mc.

If the gas has to expand against external pressure, more heat must be supplied to allow for the external work done, $\int p dv$; the capacity being now called mc' if the pressure is constant. Consequently if the gas be heated at constant pressure, from absolute zero up to the temperature T, the heat required can be expressed as—

$$H = mcT + pv = mc'T;$$

wherefore—

$$p = \rho\,(c' - c)\,T \quad \ldots \ldots \ldots \quad (2)$$

which may be called the characteristic equation of the substance.

Comparing this with the first equation, we see that—

$$u^2 = 3\,(c' - c)\,T \quad \ldots \ldots \ldots \quad (3),$$

which constitutes a definition of absolute temperature in terms of the characteristic constant $c' - c$; the "3" having reference to the three dimensions of space.

Actually to determine T we can employ equation (2), and can get rid of the constant, say, by measuring the increase of pressure when the gas is heated at constant volume. This gives—

$$\frac{dp}{p} = \frac{dT}{T};$$

or—

$$T = p\frac{dT}{dp} = \frac{1}{a} \quad \ldots \ldots \ldots \quad (4)$$

the reciprocal of the coefficient of expansion.

In other words, the expansibility of a perfect gas is simply the reciprocal of its absolute temperature.

This is consistent with the form of characteristic equation which allows for molecular bulk, though not for molecular forces—namely, $p(v - b) = RT$.

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For a slightly imperfect gas there is the cohesion or molecular-attraction term to be attended to as well, and its characteristic equation is—

$$(p + K)(v - b) = RT,$$

K being a function of volume only. For constant-volume warming this gives—

$$\frac{dp}{p+K} = \frac{dT}{T},$$

or—

$$T = p\frac{dT}{dp} + K\frac{dT}{dp},$$

or—

$$T = \frac{1}{a}\left(1 + \frac{K}{p}\right) \quad \ldots\ldots\ldots\ldots (5);$$

where a is the coefficient of expansion as measured on a constant-volume thermometer; showing that a correction factor not far from unity must be applied, depending on the incipient cohesion or inter-molecular attraction, represented by Laplace's K or van der Waal's $A\rho^2$.

To get K we must perform a definite operation, say a sudden expansion δv, under adiabatic conditions, allowing no external work to be done; and we must observe the resulting absorption of heat, say by noticing the small change of temperature δT. It would be zero if the gas were perfect. If imperfect, the energy lost is $K\delta v$.

To ensure that no external work is done, the operation must be performed in a rigid vessel, and a steady stream of gas will carry off the defect of heat δH; the cooling will then be due only to internal work $K\delta v$; and the heat change can be expressed as $mc'\delta T$, when eddies have subsided.

Thus we get—

$$K\delta v = \delta H = mc'\delta T = v\rho c'\delta T;$$

but now instead of δv we may write $-\frac{v}{p}\delta p$, since the temperature is nearly constant, so that—

$$K = -\rho c' p\frac{\delta T}{\delta p}. \quad \ldots\ldots\ldots\ldots (6)$$

Hence, denoting by θ the small observed change of temperature corresponding to the change of pressure Π, and substituting (6) in equation (5), we get finally as an expression for the absolute temperature of the gas experimented on—

$$T = \frac{1}{a}\left(1 - c'\rho\frac{\theta}{\Pi}\right) \quad \ldots\ldots\ldots\ldots (7)$$

Perhaps the equation looks still clearer if we write it in terms of the volume of air v streaming through the porous plug, down the difference of pressure δp, and carrying with it ultimately the defect of heat δH, measured anyhow; for then—

$$T = \frac{1}{a}\left(1 + \frac{\delta H}{v\delta p}\right). \quad \ldots\ldots\ldots\ldots (7')$$

But the expression for the absolute expansion term—

$$aT = \frac{p+K}{p} \quad \ldots\ldots\ldots\ldots (5')$$

is also a very simple one.

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To interpret equation (7) numerically—

The quantity $c'\rho$ will be recognised as *the atomic heat*, which is nearly the same constant for all ordinary gases, and equal in c.g.s. energy units to—

$$0{\cdot}2375 \times 0{\cdot}001293 \times (42 \times 10^6) = 0{\cdot}001294 \times 10^6 \text{ ergs per c.c., for dry air.}$$

The actual change of temperature per atmosphere, observed as the final result of the irreversible Joule and Thomson expansion, was, for air, a lowering of about a fifth of a degree, or more exactly 0·208°; so that—

$$\frac{\theta}{\Pi} = \frac{0{\cdot}208}{10^6 \text{ dynes per sq. cm.}}.$$

Hence, since *ergs per c.c.* are the same as *dynes per sq. cm.*, the value of what we have just reckoned as the dimensions of the whole term $c'\rho\theta/\pi$ come out right as a pure number (being plainly a ratio of two energies when ρ is written m/v); and the correction factor for air equals—

$$1 + 0{\cdot}001294 \times 0{\cdot}208 = 1{\cdot}00027.$$

At zero Centigrade the expansibility of air was measured by Regnault as 0·0036706. Wherefore the absolute temperature corresponding to zero Centigrade is, in accordance with equation (7)—

$$\frac{1{\cdot}00027}{0{\cdot}0036706} = 273{\cdot}17.$$

Instruments.

Of Lord Kelvin's many instrumental inventions I shall say nothing, beyond calling attention to the strongly mathematical basis on which they are founded. This fact was conspicuous to me long ago in connection with the infancy of the quadrant-electrometer—an instrument now older than most physicists, and so familiar that its unobviousness at first can hardly be appreciated; but the treatment of an electrometer as a variable condenser, which naturally led to the design of one flat surface moving over two other flat surfaces in the same plane, was, I judge, a distinctly mathematical, not an experimental, idea. It furnished at once a first approximation to the *moment* acting upon the upper flat surface, grotesquely called a "needle," and showed that the expression contained two factors—the difference of potential between the two quadrants, and the difference between their average potential and the potential of the needle above them; the needle being thereby urged to move so that the potential energy of the system should become a minimum.

Electrical Theory of Matter.

On the great modern region of physics centering round an electrical theory of matter, Lord Kelvin's mind was somewhat conservative; as perhaps it was in electricity generally, whenever results could not be obtained by straightforward dynamics or by energy calculations. In other directions he only advanced under protest, as it were, towards the goal at which others were enthusiastically working. Nevertheless, we owe to him some pioneering work even in this branch.

Comparatively modern speculation and calculation on the structure of an atom are contained in a remarkable paper by Lord Kelvin, published in the *Phil. Mag.* for 1901 under the curious title "Æpinus Atomised."

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It is reproduced in the volume of Baltimore Lectures as Appendix E. It was probably the first attempt to work out the statics of an atom, according to a simple conception whose major consequences can be traced with comparative ease, viz., that of a spherical portion of uniform positive electricity in which minute negative charges are sown like specks; being attracted towards the centre of the sphere according to the law of direct distance, and repelling each other according to the inverse square law.

Various interesting groupings can be easily calculated as stable patterns, and they tend to become more stable if they revolve regularly round the centre, or if sustained by a central group or particle. But although the calculable distribution and properties of such groups are profoundly suggestive and interesting, the behaviour of atoms of positive electricity with even a single electron inside each became instructive in the hands of Lord Kelvin.

His conception of the simplest possible electrical atom is that of a comparatively large positive uniform globe, neutralised by an equal charge of negative as a speck at the centre. Two such atoms, of course, exert no force on each other from a distance; but if they are of unequal size, and if the smaller one penetrates the bigger until the centre of the smaller is included in the circumference of the bigger, then each electron begins to be displaced, and, oddly enough, both are displaced in the same direction. If the penetration continues, both electrons enter the smaller sphere, and there adjust themselves and remain; the smaller one having robbed the bigger one of its charge, so that when they separate again the smaller one has become negative and the larger one positive. This fact is naturally supposed to correspond to some features in frictional electricity, or electrification by contact between substances of different kinds.

Lord Kelvin further goes on to calculate what would happen when one neutral atom, with an electron at centre, is approached by a small positive sphere without any neutralising electron charge. Displacement of the electron now begins long before contact; and when they approach within a certain distance, namely 1·89 times the larger radius distance between their centres, the electron in the bigger one is displaced a distance 0·63 times the radius from the centre; and there its equilibrium becomes unstable, so that it jumps across the intervening space "like a cork jumping out of a bottle" and enters the smaller sphere. It will then shoot through the smaller sphere and oscillate "perhaps ten or twenty times [or perhaps a million]," and ultimately settle down to rest at some place—not the centre—depending on the ultimate distance of the larger atom; which, however, has no power under any circumstances of regaining its charge from the smaller one. It is always the smaller that robs the bigger. This, indeed, is only a particular case of the general importance of "concentration" in the electrical theory. The mass of an electron depends upon its smallness—that is, upon its potential as well as upon its charge—and could be made enormous if it were assumed small enough; though, as we well know, to account for its actual mass a definite smallness is appropriate.

It is confessedly unlikely that an atom should have only one electron, but that which it is fairly easy (not too easy) to calculate for this simple case would happen in modified fashion in more complex cases, when the electrons were more numerous; and a vast number of possibilities suggest themselves, such as with ingenuity can be made to account for a great variety of the fundamental facts of chemistry. Ingenuity such as is needed for this difficult work, which at present is only in its infancy, has been conspicuously displayed in various well-known writings of Professor J. J. Thomson.

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Meanwhile to return to Lord Kelvin.

Where there are more than one or two electrons in the atom, constituted as supposed above, they distribute themselves in stable form as follows—

Three form an equilateral triangle.

Four are at the corners of a regular tetrahedron.

Five may permit four to be in a plane, at the corners of a square, with one centrally perpendicular to the plane of the square, though more certainly stable if three are in a plane and two are on its central perpendicular, one on each side.

Six are stable at the corners of a regular octahedron; they are also possibly stable in a plane if one is at the centre and five at the corners of a pentagon.

Eight can be at the corners of a cube, but with insecure stability, unless there are some at the centre too.

Twenty, at the corners of a regular dodecahedron, would either have to be *constrained* to lie on a spherical surface, or else would have to be well sustained by repulsive forces from the interior.

The calculation for space-distribution becomes complicated, and most attention has been paid to distribution in a plane; wherein the criteria for stability, as depending either on central repulsion, or on centrifugal force due to regular rotation, has been admirably worked out by J. J. Thomson in a methodical and very instructive way.

A typically instructive and simple case is that of four electrons revolving round the centre. So long as they are revolving above a certain angular speed, they are stable when at the corners of a square; but if the speed falls below a critical value this grouping becomes unstable, and they fall, with a convulsion and emission of energy, into a statical position of equilibrium at the corners of a tetrahedron.

It is in a direction typified by this simple example that we are looking for an explanation of some part of the phenomenon of spontaneous radio-activity.

Cosmic Calculations.

Of the work of Lord Kelvin in elasticity, I shall here say nothing beyond the remark that his kinetic view of elasticity often seems to me one of the most suggestive and ultimately pregnant of all his theories. And as partly said before, I must omit all reference to his work on the size of atoms, on capillarity, and on the tides.

His papers on celestial dynamics are very remarkable and lucid, though we may not feel that they represent the last word on the question; any more than the last word has been said as to the age of the sun or of the earth. I shall refer specially to his Paper estimating the amount of matter in the sensible universe, on the basis of accounting for the stellar velocities met with, and the darkness of the stellar sky. In this Paper he argues that the average density of matter in the universe must ultimately be infinitesimal; he reckons what it is in the space at present accessible to our aided senses; and he conceives of this cosmos as formed by a clash of atoms. There has now appeared a posthumous Paper of his on a similar sort of subject, which looks as if it had been a preliminary arithmetical calculation preparatory to his paper on Gravitational Clustering. In this paper the 6,000 trillion tons of the earth's mass are supposed to be distributed regularly in cubic order, as cubic tons at rest throughout a vast space, and are then allowed to approach, under mechanical and easily reckoned conditions, until they simultaneously clash. This

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sort of procedure is plainly preliminary to an attempt to visualise the formation of a cosmos by a regulated and definite variety of the concourse of atoms.

At the Glasgow Meeting of the British Association in 1901 Lord Kelvin gave a most interesting abstract of his cosmic papers in the *Philosophical Magazine* for the same year; and parts of this are so characteristic of his mode of thought, and yet so comparatively easy to read, that I would call general attention to it. It is reproduced as Appendix D to the volume of his Baltimore Lectures, and may be abstracted further thus—

He begins by discriminating matter from ether, without denying that ether is material. [He chooses to do this by speaking of "gravitational matter"; but it is much simpler to employ the two terms "matter" and "ether" and to keep them distinct.]

He then takes his favourite sphere, of radius 3×10^{16} kilometres—being the distance at which a star has a parallax of one-thousandth of a second—and supposes distributed uniformly through it the mass which he images actually to exist within it, namely, one thousand million times the sun's mass. The main reason for postulating such a mass as that, is that by gravitational attraction it would give, in process of time, something like the stellar velocities which are actually observed; whereas a mass ten times as great would generate velocities much greater than any known stellar velocity. Actual stellar velocities could be generated under favourable conditions by such a mass, even though it were uniform. In so far as it was non-uniform—as of course it really is—the velocities generated would tend to be in places greater.

The density of matter in the above visible universe amounts to only $1{\cdot}6 \times 10^{-23}$ grammes per cubic centimetre; and if the whole mass were reduced to globules 2 centimetres in diameter, and of the sun's mean density, each globule would have 360 million cubic kilometres of space surrounding it; and the visual obstruction to an eye at the centre of such a set of globes, to light coming from outside, would only be $\frac{1}{3^{17}}$.

He then makes an important digression on the brightness of the star-lit sky, and reckons that in order to make up with such disks anything like the solar brightness—to make, say, 3·87 per cent. of the whole sky bright with stars—the radius of a sphere thus full of matter at this density must be enlarged to 3×10^{27} kilometres. But then, with this radius, light would take 3×10^{14} years to travel from circumference to centre; and the life of any luminary is not likely to be greater than one hundred million years—it is probably less. So, since the time taken by light to travel from the outlying stars to the centre of such a gigantic sphere is three million times the life of any star considered as a luminous body, it follows that the greater part of the stars in such a globe as that would be dark, their luminous epoch being a mere episode in their total history. So that even this extension of the cosmos would fail to illuminate the sky.

He next reduces all the matter in the supposed universe to atoms, distributed uniformly throughout the originally assumed space with radius 3×10^{16} kilometres, and reckons what happens when they begin and continue to fall together, starting with the density of $1{\cdot}6 \times 10^{-23}$, and shrinking by mutual gravitation, without any ethereal friction or other disturbance. In that case, he says, they would "take nearly 17 million years to reach 0·0161 of the density of water, and about two hours longer to shrink to infinite density at its centre." [This is a quite characteristic sentence.] At the time when it reached the above-specified fraction of the density of water the velocity of the particles would be comparable with that of light, and in a moderate number of seconds "the whole surface of our condensing globe of gas or

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vapour or crowd of atoms would begin to glow, shedding light inwards and outwards."

And he then concludes thus :—

"To come to reality, according to the most probable judgment present knowledge allows us to form; suppose at many millions, or thousands of millions, or millions of millions of years ago, all the matter in the universe to have been atoms very nearly at rest or quite at rest, more densely distributed in some places than in others, of infinitely small average density through the whole of infinite space. In regions where the density was then greater than in neighbouring regions the density would become greater still; in places of less density the density would become less; and large regions would quickly become void, or nearly void, of atoms. These large void regions would extend so as to completely surround regions of greater density. In some part or parts of each cluster of atoms, thus isolated, condensation would go on by motions in all directions not generally convergent to points, and with no perceptible mutual influence between the atoms until the density becomes something like 10^{-6} of our ordinary atmospheric density, when mutual influence by collisions would begin to become practically effective. Each collision would give rise to a train of waves in ether. These waves would carry away energy, spreading it out through the void ether of infinite space. The loss of energy thus taken away from the atoms would reduce large condensing clusters to the condition of gas in equilibrium under the influence of its own gravity only, or rotating like our sun or moving at moderate speeds as in spiral nebulæ, &c. Gravitational condensation would at first produce rise of temperature, followed later by cooling and ultimately freezing, giving solid bodies, collisions between which would produce meteoric stones such as we see them. We cannot regard as probable that these lumps of broken-looking solid matter (something like the broken stones used on our macadamised roads) are primitive forms in which matter was created. Hence we are forced, in this twentieth century, to views regarding the atomic origin of all things closely resembling those presented by Democritus, Epicurus, and their majestic Roman poetic expositor, Lucretius."

The fact that after a lifetime of immersion in all the intricacies of Natural Philosophy Lord Kelvin still postulated an origin or beginning for the material universe—a beginning when it was essentially different, not only locally but universally, from its present condition—and that he endeavoured to conceive what it might then have been like, in those early times—is a notable circumstance and one of general interest. To me there appears no reason for calling those times "early" rather than "late"; nor would I suppose a beginning or ending at all, either for space or for what is in space, other than such beginnings or endings as we might detect, or may hope to detect, somewhere, even now. But Lord Kelvin clearly thought otherwise; so with this notable aspect of his life-work I conclude my address.

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HYDROLYSIS AS ILLUSTRATED BY HEATS OF NEUTRALISATION.

By V. H. VELEY, D.Sc., F.R.S.

(*A Paper read before the Faraday Society, Tuesday, February* 25, 1908, DR. T. M. LOWRY *in the Chair.*)

"Nam certe neque consilio primordia rerum
Ordine se suo quæque sagaci mente locarunt
Nec quos quæque darent motus pepigere profecto
Sed quia multa modis multis mutata per omne
Ex infinito vexantur percita plagis."

LUCRETIUS (DE RERUM NATURA)

"And I saw the flaring atom streams
Ruining along the illimitable inane
Fly on to clash together again and make
Another and another frame of things
For ever."

TENNYSON (LUCRETIUS).

Numerous determinations of the heat of neutralisation of bases with mineral, and especially hydrochloric acid, have been collected by Berthelot,* Thomsen,† Luginin,‡ Alexèeff,§ and others. But for the most part they have for the past twenty years remained consigned to physico-chemical tables as of no special interest, possibly because experimental data have been viewed too exclusively from the standpoint of ionic dissociation and velocities. On the other hand, numerous determinations have been collected of the hydrolysis values of the hydrochlorides of bases by various methods, such as: (i.) the conductivity of solutions of the salts themselves (Bredig ||) or of the salts, formed in solution, with addition of excess of acid on base (Walker ¶); (ii.) the catalysis of methyl acetate (Walker, Winkelblech,**); (iii.) the hydrolysis of cane sugar (Walker ††), and other methods, some of equal, and others of less accuracy.

In the present communication it is desired to correlate, so far as data permit, hydrolysis values with those of heats of neutralisation as formulæ proposed to calculate out the latter from determinations of the former have raised interesting and important issues.

* *Thermo Chemie Tome*, **1**, 1, Paris, 1897.
† *Thermo Chemische Untersuchungen*, Bd. 2, Leipzig (1882).
‡ *Ann. Chem. Phys.* [5], **17**, 263 (1879).
§ *Bull. Soc. Chem.* [3], **2**, 717 (1889).
|| *Zeits. f. Physikal Chem.*, **13**, 191 (1894).
¶ *Ibid.*, **4**, 316 (1889).
** *Ibid.*, **36**, 546 (1901).
†† *Journ. Chem. Soc. Trans.* 576 (1895). The literature relating to hydrolysis values has been collated by Lunden, *Zeits. f. Physikal Chem.*, **54**, 560 (1906).

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The following symbols will be used throughout the paper :—

μ = Specific conductivity.
Λ = Equivalent conductivity.
v = Dilution litres/gram. Equivalents = 1/N.
K_b = Ionic constant of bases.
K_w = Concentration of ions of water.
x_v = Hydrolysis value of salt at dilution v (the values of x are multiplied by 100 to express the results in terms of percentages).
Q (neutr.) = Heat of neutralisation expressed in 100 gram.-calories.
T = Absolute temperatures.

The following formulæ are implied in the text or calculations :—

$$x = \frac{M(\Lambda)_v - \mu(\Lambda)_v}{\mu(\Lambda)_{HCl} - \mu(\Lambda)_v} \text{ (Walker *)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Though this is of not very general applicability owing to difficulties in determining directly $\mu(\Lambda)_v$, conductivity of nonhydrolysed salt—

$$\frac{K_b}{K_w} = \frac{(1-x)v}{x^2} \text{ (Arrhenius †)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This formula is more generally applied to calculate out either K_b or $\frac{K_b}{K_w}$ taken as constant for one temperature.

From the Nernst equation—

$$Q = RT^2\epsilon \frac{d \log^{10} K}{dt} \text{ (‡)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

taking $R = 1{,}985$ expressed as work, gram.-calories and $\epsilon = 2{,}3046$ as work per volt gram.-calories, we have—

$$Q = 1{,}985 \times 2{,}3026 (= 4{,}571) \frac{d 10^{10} K}{dt} \quad (3 \text{ bis}).$$

Substituting $\frac{K}{K_b}$ for K, it is possible to calculate out the heat of neutralisation, provided K_b has been determined at more than one temperature, as we have by integration of (3)—

$$\log KT_1 - \log KT_2 = -\frac{a(T_1 - T_2)}{4{,}571\, T_2 T_1} - \frac{b}{1{,}985} (\log T_1 - \log T_2).$$

For the purpose of calculation the values of K_w are deduced from Kohlrausch and Heydweiller's § table :—

Temp.	10°	15°	25°	40°
$K_w 10^{14}$	0·31	0·49	1·11	3·26

The values of K_b are taken direct or calculated from the results of Bredig || [Br], Winkelblech || [Wi], Walker || [Wa], Lunden ¶ [L], and those of myself [V] by the methyl-orange method described at present in outline.**

* *Loc. cit.* (6).
† *Zeits. f. Physikal Chem.*, **5**, 17 (1890).
‡ *Zeits. f. Electrochemie*, **12**, 1 (1906). *Cf.* Berthelot, *ibid.*, **10**, 621 (1904). Recommendations of Units Commission of Deutsches Bunsen Gesellschaft.
§ *Wied. Ann.*, **53**, 235 (1894).
|| *Loc. cit., supra.*
¶ *Loc. cit., supra.* and *Meddelanden fr. k. Vetenskapsakadamien Nobel Institut*, Bd. 1, Nos. 7 and 8 (1907).
** *Journ. Chem. Soc. Proc.*, 284 (1907).

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Unfortunately, there are important lacunæ: either the heats of neutralisation have not been determined, or the dilution and initial temperature omitted in cases in which numerous hydrolysis values are available, and, on the other hand, the former have been determined, but not the latter. It is hoped that the present communication may, by directing attention, lead to the filling up of such lacunæ.

HYDROCHLORIDES.

Bases not containing Carbon.

	Ammonia.	Hydroxylamine.
Q (neutr.)	122·7	92
x	Inappreciable	2·58 [1024] Wi 8 [1 × 104] V
K_b	2·3 10^{-3}	[25°] 7·33 10^{-9} Wi [15°] 6·5 10^{-9} V

The above results need no explanation; ammonia with a high heat of neutralisation correlated with a high basic constant and inappreciable hydrolysis of its hydrochloride at ordinary temperature, and hydroxylamine with also a relatively high heat of neutralisation, though 30 units less than ammonia, correlated with a lower basic constant and ion hydrolysis value.

Hydrazin.—

Q (neutr.)	96·5
Q + 1st mol. HCl	96·0
Diff. Q + 2nd mol.·HCl	0·5
x	[48·5] [1024] Br [51·5] [2 × 104] V

The thermochemical data of Bach * given above show that practically the whole of the heat is evolved on addition of the first molecular proportion of hydrochloric acid, that of the second being inconsequent. Bredig (*loc. cit.*) concluded from his results that the specific conductivity of solutions of the dihydrochloride is practically equal to that of a mixture in equimolecular proportion of the monohydrochloride and hydrochloric acid ($v = 32$ to $v = 1032$), thus showing that the dihydrochloride is hydrolysed up to 50 per cent. (the actual figure being 48·5 per cent.). My results gave a value 51 per cent. ($v = 4 \times 10^4$ to 8×10^4). These values are within the limit of experimental error, and the change may therefore be represented thus:—

$$ClH_3N.NH_3Cl + HOH = ClH_3N.NH_3OH + HCl,$$

the combination ClH_3N being of an order comparable to ClH_4N. It is evident that since the hydrolysis value is identical at $v = 32$ or $v = 80{,}000$ Arrhenius' dilution formula is not applicable in such a case. Hydrazin is further remarkable in that the presence of NH_2 grouping combined with a N atom *decreases* the affinity value (relatively to ammonia), thus resembling a diacidic base in which a second NH_2 grouping is attached to a C atom in a hydrocarbon residue, whereas in all other cases the presence of a second NH_2 grouping attached to a N atom increases the affinity value. Bredig's explanation † that this difference is a necessary consequence of the contiguity of the two NH_2 groupings may possibly be open to question.

* *Zeits. f. Physikal Chem.*, 9, (250) 1892.

† *Cf.* Trevor, *ibid.* 10, 3 (1892). and Noyes *ibid.* 11 495 (1893)

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The hindrance caused by the introduction of a NH_2 grouping attached to a N atom is well illustrated by a comparison of the pair of substances given below :—

	Urea.	Semicarbazide.
Q (neutr.)	Inappreciable	(?)
x	90·5[10] Wa	10·9 [1 × 10⁴] V
K_b	[40°] 3·8 10^{-14}	[15°] 9·1 10^{-9}

Taking the value of K_b for urea at 15° as at 1 10^{-14} as an approximate figure the introduction of the NH_2 grouping increases the basic value by nearly 91,000.

Recently I have obtained similar results with guanidine and amino-guanidine.

Paraffinoid Amines.—

	Methylamine.	Dimethylamine.	Trimethylamine.
Q (neutr.)	130·0	110	89
x	nil	nil	trace at $v = 4 \times 10^3$
K_b	5·10^{-2} Br	7·4 10^{-2} Br	7·4 10^{-3} Br

Of these bases trimethylamine with the lowest heat of neutralisation is the only one in which hydrolysis of the hydrochloride could be detected.

	Ethylamine.	Ethylene Diamine.
Q (neutr.)	132	(+ 1st mol. HCl) 235 / 125 Diff. (2nd mol. HCl) 110
x	nil	0·6 [4 × 10³]
K_b	[25°] 5·6 10^{-2} Br	[15°] 5·9 10^{-7} V

Bredig from his determinations concluded that ethylene diamine dihydrochloride showed only traces of hydrolysis at $v = 1{,}032$, my experiments gave a very low value, but this is sufficient to show the decrease of basic function produced by the introduction of a NH_2 grouping attached to a C atom, and that the second molecular proportion of hydrochloric acid with its lower heat of neutralisation, though even of a high value, undergoes this trace of hydrolysis.

Paraffinoid Aminocarboxylic Acids.—These substances, as belonging to the class of amphoteric electrolytes, have received considerable attention as regards their basic and acid constants, but, unfortunately, thermochemical data are not very numerous.

HYDROCHLORIDES.

	Glycine.	Alanine.
Q (neutr.)	10	9
x	83·6 [1024] Wi 86·0 [4 × 10⁴] V	80 [1024] Wi
K_b	[25°] 2·33 10^{-12} Wi [15°] 1·02 10^{-12} V	[25°] 5·14 10^{-12} Wi

The heats of neutralisation of the above with hydrochloric acid are about one-eleventh of that of ammonia, more than 80 per cent. of their hydrochlorides are hydrolysed, and their basic constants reduced in round figures by 1 10^{-9}, or one hundred-millionth.

The heats of neutralisation of these substances with soda and their acid constants show similar relationships, as shown below :—

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SODIUM SALTS.

	Glycine.	Alanine.
Q (neutr.)	30	25
x	17·2 [1024] Wi	17·3 [1024] Wi
K_a	[25°] 1·8 10^{-10}	[25°] 1·8 10^{-10}

The values of Q (neutr.) of these acids is approximately one-fifth of that of soda with hydrochloric acid, and relative thereto their acid constants reduced to a low figure.

The relationships of asparaginic acid are of similar order, but as the experiments of Walden * and myself † show irregularities, not as yet explained, it is thought best to omit the figures.

Benzenoid Amines.—Aniline: Lunden ‡ has recently determined the values of K_b for this base at different temperatures, the necessary condition for the application of Nernst's formula, and his results are given below :—

	15°	25°	40°
K_b	3·06 10^{-10}	4·57 10^{-10}	7·56 10^{-10}

On compounding the first and second values (mean temperature 20°) and the second and third values (mean temperature 32·5°), the calculated values by Nernst's formula are Q (neutr.) 71·1 and 72·5 respectively. The values of Q (neutr.) obtained by Luginin 75·1 and Vignon 75·5, as corrected for hydrolysis, are in fair accordance with the calculated values.

The values of K_b deduced from those of $x = 14{\cdot}4$ at $v = 1025$ (temp. 25°) Br, and $x = 32{\cdot}2$ at $v = 1 \times 10^4$ (temp. 18°) V, agree with those given above.

Methyl and Dimethyl Anilines.—The statements of various authors as to the basic constants are rather discrepant; Bredig's and my results are more in accordance with the heats of neutralisation.

	Aniline.	Methylaniline.	Dimethylaniline
Q (neutr.)	75	69	68

Bredig (*loc. cit.*) gives the order as regards their ionic velocities :—

Aniline > Methylaniline > Dimethyaniline.

The values of x and K_b resulting from my experiments are as follows :—

	Aniline.	Methylaniline.	Dimethylaniline.
x	32·2 [1 × 104]	37·5 [1 × 104]	36·0 [1 × 104]
K_b	[18°] 3·2 10^{-10}	[18°] 2·55 10^{-10}	2·42 10^{-10}

The order is—

Aniline > Methylaniline = Dimethylaniline

which is practically that of the heats of neutralisation.

SUBSTITUTED ANILINES.

Chloranilines.—At present I am engaged upon the hydrolysis of the three isomeric monochloranilines, the heats of neutralisation of which have been measured with the following results :—

	o Derivative.	*m* Derivative.	*p* Derivative.
Q (neutr.)	63	66	72

* *Zeits. f. Physikal Chem.*, 8, 411 (1891).
† *Journ. Chem. Soc. Trans.*, 161 (1907). *Cf.* (14).

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The probable order of the values of K_b will be—

$$p > m > o \text{ derivative,}$$

which, as will appear in the sequel, holds good for other amino-derivatives of benzene.

Nitranilines.—In the case of these derivatives the heat of neutralisation of the *p* derivative only has been determined, but the values of K_b for all of them has been measured.

	o Derivative.	*m* Derivative.	*p* Derivative.
Q (neutr.)	(?)	(?)	18
K_b	$1{\cdot}5\ 10^{-14}$	$1{\cdot}2\ 10^{-12}$	$4\ 10^{-12}$

The order of value of these derivatives is that given above.

Benzylamine and the Toluidines.

The following values have been obtained :—

	Benzylamine.	*o* Toluidine.	*m* Toluidine.	*p* Toluidine.
Q (neutr.)	129	—	—	76
x	nil	17·3 [1024] Br 40·6 [1 × 104] V	12·3 [1024] Br	8·33 [1024] Br 28·1 [1 × $4-10^4$] V
K_b	$2{\cdot}4\ 10^{-3}$ Br	[25°] $3{\cdot}2\ 10^{-10}$ [15°] $1{\cdot}52\ 10^{-10}$ V	[25°] $6{\cdot}1\ 10^{-10}$	[25°] $14{\cdot}10^{-10}$ [15°] $4{\cdot}5\ 10^{-10}$ V

Benzylamine, both as regards its heat of neutralisation and value of K_b, behaves as a paraffinoid amine CH_2XNH_2; the order of values of the toluidines is—

$$p > m > o \text{ derivative.}$$

Phenylene Diamines.—Bredig (*loc. cit.*) showed that these compounds, as hydrazin, are hydrolysed at dilutions $v = 64$ to $v = 2{,}048$ approximately to the monohydrochloride and hydrochloric acid, thus—

$$ClH_3N\ C_6H_4 \cdot C_6H_4\ NH_3Cl\ HOH = ClH_3N \cdot C_6H_4 \cdot C_6H_4\ NH_3OH + HCl.$$

My own results obtained at far greater dilutions ($v = 4 \times 10^4$ to 8×10^4) confirm his conclusions fully; both are in accordance with thermochemical data.

	o Derivative.	*m* Derivative.	*p* Derivative.
Q (neutr.)	101	117	147
Q (+ 1st mol. HCl) ...	70	70	88
Diff. Q (+ 2nd mol. HCl)...	31	47	59
x	ca 50 Br	ca 50 Br	ca 50 Br
	44·4 } V 50·0 }	45·3 } V 48·4 }	43·7 } V* 47·0 }

If only the second molecule of hydrochloric acid is removed largely by hydrolysis, then the order according to the heats of neutralisation should be—

$$p > m > o \text{ derivative,}$$

which is that of the second row of figures of my determinations. But there is some evidence that the hydrolysis of the first molecule of hydrochloric acid commences before that of the second molecule is completed, precisely as in the case of certain dicarboxylic acid † the ionisation of one carboxlyic grouping commences before that of the other is completed.

* The values of *x* of the upper line were obtained by diluting the original solutions directly, of the lower line by heating the original solutions for two hours at 60°, and then subsequently diluting.

† *Cf. Zeits. f. Physikal. Chem.*, **3**, 380 1889), and **57**, 159 (1906).

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Phenyl Hydrazin.—This base, generally regarded as a substituted hydrazin, behaves, both as regards its heat of neutralisation value and its basic constant, as an amino-aniline $N(NH_2)HC_6H_5$, and, like aniline, it combines only with one molecular proportion of hydrochloric acid to form probably the compound $N(NH_2)C_6H_5H_2Cl$.

The following results have been obtained :—

Q (neutr.)	82
x	14·8 [4 + 104] V
K_b	[15°] 1·62 10−9 V

Thus the introduction of a second NH_2 grouping attached to a N atom in aniline, as in guanidine, increases both the value of Q (neutr.) and of K_b.

The Amino-benzoic Acids.—These substances, as the amino-acetic acids, have received considerable attention ; the following values have been obtained :—

HYDROCHLORIDES.

	o Derivative.	*m* Derivative.	*p* Derivative.
Q (neutr.)	(?)	27·5	(?)
x	86·9 [1024] Wi	55·7 [1024] Wi	81·2 [1024] W
K_b	[25°] 1·37 10−12	[25°] 1·20 10−11	[25°] 2·33 10−12

In the case of these acids the order is—

$$m > p > o \text{ derivative.}$$

SODIUM SALTS.

Q (neutr.)	105	121	92·7
K_a	[25°] 1·06 10−5	[25°] 1·63 10−5	[25°] 1·10 10−5 *

Here the order is as regards thermochemical data $m > o > p$, but as regards the acid constants $m > p > o$, there is clearly need of revision.

Much work is still required to be done on the heats of neutralisation of the amino-phenols with hydrochloric acid, the basic constants of some of which I have recently determined, as also of acid constants of the phenols and the three isomeric nitro-phenols. The heats of neutralisation of these last have been determined by Alexèeff and Werner (*loc. cit.*) and Luginin (*loc. cit.*). Lunden has recently determined the values of K_a for the *p* derivative at different temperatures, and from them by the Nernst formula has calculated out the value of Q (neutr.) for soda ; this is 87·3 at 25°, which agrees within the limit of experimental error with the value 87·1 found by Alexèeff and Werner.

Naphthalene Derivatives.—It is remarkable that notwithstanding the commercial importance of these compounds, so few of the requisite data are available for the purpose of comparison.

Pyridine Derivatives.—Pyridine: From the values of K_b determined at different temperatures Lunden has likewise calculated the value of Q (neutr.) as at 58·2 at 25°, which is only in general agreement with the values found by Berthelot, 51·0 at 22°, and by Colson, 52·0 at 14°. If the mean is taken we have—

Q (neutr.)	55
x	26·1 [2 + 104] V
K_b	[13°] 1·06 10−9 V [10°] 1·06 10−9 L

It is worthy of observation that notwithstanding the general accordance of the results, pyridine with a comparatively *low* value for heat of neutralisation should, as regards its hydrochloride, show a comparatively *high*

* Johnston-Cumming, *Proc. Roy. Soc.*, 78A, 82 (1906).

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hydrolysis value and basic constant, in round figures three times greater than aniline.

Piperidine.—This base, formerly regarded as a hexahydropyridine, is remarkable in that the values of the heat of neutralisation Q (neutr.) = 133° (equal to that of sodium hydroxide), and of its basic constant $K_b = 1{\cdot}58\ 10^{-1}$ are higher than that of all other nitrogen containing bases. Further, I have been unable to detect any traces of hydrolysis of its hydrochloride, whether in concentrated or dilute solutions.

Its constitution is probably, therefore, that of a hexamethylene imine, and points to the necessity of a study of the hydrolysis and basic constants of the amino-derivatives of closed chains of CH_2 groupings.

Quinoline Derivatives.—Here, again, very few data are available except for the parent base.

Quinoline—

$\varkappa$	15·6 [1 × 10⁴] V 2·1 [3 × 10¹] Wa
K_b	[15°] 3·4 10⁻⁹ V [60°] 7·4 10⁻⁹ Wa

My recent experiments have shown that tetrahydroquinoline resembles piperidine in that its hydrochloride shows no trace of hydrolysis. But there is wide field for the investigation of the physical constants of the derivatives of these bases, especially having regard to their relationship with the cinchona alkaloids, which are remarkable in that they are for the most part mono-acidic towards hydrochloric acid (and these monohydrochlorides show no trace of hydrolysis), but di-acidic towards sulphuric acid.

Metallic Chlorides.—It further appears that observations are required upon the hydrolysis at considerable dilutions of certain of these substances, such, for example, as that of cadmium Q (neutr.) = 101·5, which even in concentrated solutions shows irregularities as regards its transport numbers,* and equivalent conductivities,† as also of zinc Q (neutr.) = 99·4. It is further probable that ferric chloride Q (neutr.) = 55·8 and aluminium chloride Q (neutr.) = 93·2 ‡ are hydrolysed to a greater or less degree into the hydroxides and hydrochloric acid; but no exact determinations have been made for the former, while in the case of the latter the results of Ley § and Bruner,‖ made under such different conditions, lead to results which appear discordant.

So also sodium silicate in aqueous solution consists largely of sodium hydroxide and silicic acid,¶ ammonium borate of ammonium hydroxide and boric acid,** and numerous other examples might be cited.

It is evident, therefore, that a wide field of investigation is open, and it is hoped that this contribution may not only serve as a record, however imperfect, of results already achieved, but also may awaken interest in the correlation of hydrolysis with thermo-neutrality.

Finally, I have to express my obligations to Dr. Harald Lunden of the Nobel Institut, Stockholm, for his courtesy in sending me his publications, as also private correspondence; from both of these sources I have obtained considerable assistance in drawing up the present communication.

* Hittorf, *Pogg. Ann.*, **98**, 1 (1856).
† Grotian, *Wied. Ann.*, **18**, 177 (1883).
‡ Kohlrausch-Holborn, *Leitvermögen der Electrolyte*, p. 109 (Leipzig, 1898).
§ *Zeits. f. Physikal Chem.*, **30**, 218 (1897).
‖ Ibid., **32**, 132 (1900).
¶ Kohlrausch, *Wied. Ann.*, **47**, 756 (1892).
** Lunden, *loc. cit.* (14), Bd. 8, 24 (1907).

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DISCUSSION.

Dr. G. Senter asked if Dr. Veley was of opinion that there is a direct connection between heats of neutralisation and degree of hydrolysis of such a nature that the smaller the heat of neutralisation the greater the hydrolysis. Although not expressly stated, it appeared from the context (*e.g.*, methyl and dimethyl anilines, p. 5) that this was the general idea underlying Dr. Veley's paper.

It is very doubtful, however, if there is any such relationship as that assumed. The neutralisation of a strong base MOH by a weak acid HA may be represented as taking place in the following two stages—

(1) $HA = H^{\cdot} + A' \pm x$ cal.
(2) $H^{\cdot} + A' + M^{\cdot} + OH' = M^{\cdot} + A' + H_2O + 13{,}700$ cal.

The heat evolved depends, therefore, on the heat of dissociation of the acid, and, as Arrhenius has shown, there is no direct connection between the strength of an acid and its heat of dissociation—the latter may be positive or negative. The following numbers for the heats of neutralisation of hydrochloric acid (very strong), hydrofluoric acid (moderately strong), and acetic acid (very weak), by sodium hydroxide, show this conclusively—

$HCl + NaOH = NaCl + H_2O + 13{,}700$ cal.
$HF + NaOH = NaF + H_2O + 16{,}300$ cal.
$CH_3COOH + NaOH = CH_3COONa + H_2O + 13{,}400$ cal.

Dr. Veley appears to suggest that the smaller heat of neutralisation in the case of a weak base (or acid) depends partly on incomplete neutralisation. This effect, however, is, in general, small even for very weak bases and acids. It can readily be calculated that when aniline ($k_b = 4{\cdot}9 \times 10^{-10}$ at 25°) is neutralised by hydrochloric acid in molar solution, neutralisation is complete within about ½ per cent.

The heat of neutralisation is a complicated phenomenon and appears to be influenced by the following factors among others: (1) differences of hydration before and after neutralisation; (2) change in molecular complexity, *e.g.*, hydrofluoric acid; (3) heats of dissociation of the acids and bases concerned; (4) incomplete neutralisation, when the acids or base is *very* weak, or when the reaction takes place in very dilute solution.

Mr. F. E. Pollard, with reference to Dr. Veley's statement that measurements of variations in electrical resistances could not be relied on when the degree of dilution exceeded one part in 20,000, mentioned that he had recently been engaged in experimental work with a new apparatus with which conductivities were determined definitely, in the cases of certain haloid salts and some others, in solutions containing only one part in half a million. It was possible that at no distant date this apparatus might be exhibited at a meeting of the Society.

Dr. A. C. Cumming asked the author how he was able to get his water sufficiently pure when working at very extreme dilutions. The practical difficulties on this account must have been considerable.

Dr. V. H. Veley, in reply, admitted that the heat values obtained by addition of acids to bases were made up of numerous factors, some of which were, as yet, imperfectly understood. The correction to be applied for hydrolysis to the heat of neutralisation of aniline and hydrochloric acid for the determinations of Luginin and Vignon amounted to 1 per cent. But, however all this might be, it appeared from the very large number of cases examined that the higher the value for heat of

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neutralisation composed of all its factors, the less the hydrolysis value, and conversely. It was true that there were certain exceptions not readily explained by formation of stable hydroxides, &c., such, for example, as pyridine (p. 7), and the speaker had observed that aqueous solutions of its hydrochloride required a long time before final equilibrium set in of the system—

$$\text{Base (diss.)} + \text{HCl (diss.)} \rightleftharpoons \text{salt (diss.)}$$

As regards the effect of impurities in the solutions used the method adopted by the author eliminated that of dissolved carbonic acid, which is the main source of error in conductivity determinations, but substances extracted from glass surfaces remained a difficulty, and it was found necessary to accustom or train the glass to the solution to be contained therein. The effect of greasy matters was quite disastrous, and the author reiterated his views expressed elsewhere, that these were mainly due to the slime of certain water bacteria, which distils over with the steam even though the bacteria themselves have been presumably destroyed by the process of boiling.

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A STUDY OF THE SULPHUR ANION AND OF COMPLEX SULPHUR ANIONS.*

By JOSEPH KNOX, D.Sc. (Carnegie Research Fellow of Aberdeen University; late 1851 Exhibition Research Scholar). *Communicated by* Dr. A. C. CUMMING.

(*A Paper read before the Faraday Society on Tuesday, February 25, 1908, Dr. F. MOLLWO PERKIN, Treasurer, in the Chair.*)

I. THE COMPLEX-FORMATION BETWEEN HgS AND Na_2S.

A. *Solubility of Black and of Red HgS in Na_2S Solutions.*—The solubility of HgS in Na_2S solutions is due to the formation of a complex anion according to the following general scheme—

$$m\,HgS + n\,S'' \rightleftarrows (HgS)_m\,(S'')_n.$$

Since HgS is practically insoluble in NaHS solutions, we may conclude that of the two ions of hydrogen sulphide (HS′ and S″) only the S″-ions take part directly in the process. From a study of this reaction, then, the concentration of the S″-ions may be determined, and hence conclusions may be drawn as to the constitution of sulphide solutions.

For equilibrium, the law of mass-action gives the equation—

$$[(HgS)_m(S'')_n] = K\,[HgS]^m\,[S'']^n. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The square brackets denote the concentration, in moles per litre, of the enclosed molecules. K is the stability-constant of the complex anion, and represents the concentration of the latter when that of the "neutral part" and of the "simple ion" † are made unity. This condition cannot, of course, be realised in the present case.

The equation shows that the concentration of the complex anion depends only on the complex-constant and on the concentrations of the "neutral part" and of the "simple ion."

In saturated solutions the concentration of HgS, which is present also as a solid phase, is constant; in this case, therefore, the concentration of the complex is proportional to $[S'']^n$. Now, Küster ‡ has shown that Na_2S in aqueous solution is to a very large extent hydrolysed into NaHS and NaOH, and since it is the salt of a weak acid and a strong base, this hydrolysis must increase with dilution. The relative concentration of the S″-ions must, therefore, diminish with dilution, and, as the solubility of HgS depends on the S″-ion concentration, we may expect that the ratio of HgS dissolved to Na_2S will also diminish with the dilution. This conclusion is confirmed by the experimental results (see Table I.).

The Na_2S solutions used in this investigation were partly made from crystallised Na_2S (Kahlbaum), and partly from NaOH, prepared from sodium, according to Küster's method,§ and were preserved under an

* A preliminary notice appeared in the *Zeitschr. für Elektrochemie*, 1906, **12**, 747.
† Abegg and Bodländer, *Zeitschr. f. anorg. Chemie*, 1899, **20**, 471
‡ *Zeitschr. f. anorg. Chemie*, 1905, **43**, 53.
§ *Zeitschr. f. anorg. Chemie*, **41**, 447.

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atmosphere of hydrogen, as recommended by him. All operations were performed, as far as possible, in an atmosphere of nitrogen, so as to avoid the oxidation of the solutions by atmospheric oxygen. All experiments were performed in a thermostat at 25° C. The red HgS used was cinnabar from Kahlbaum, and in the solubility determinations was shaken with the sulphide solution in a glass bottle with ground-in glass stopper till two consecutive analyses agreed within the limits of experimental error. The time of shaking was in the majority of cases about three days, which was found ample for the establishment of equilibrium even in the case of the most dilute solutions. For the analyses, the bottles were hung in the thermostat till the solid had completely settled. Measured quantities of the clear solution (5 to 50 c.c., according to the dilution) were then pipetted out, diluted with water, acidified with HCl, and H_2S passed in for a short time to complete the precipitation of the HgS. The precipitate was collected in a Gooch's crucible, washed thoroughly with water, then with alcohol, and finally with carbon disulphide to remove traces of sulphur, and dried at 105°–110°. In the case of the more concentrated solutions dilution with water at once precipitated the greater part of the HgS as the black modification, while in the more dilute solutions it was deposited more slowly.

The solutions of HgS in Na_2S are yellow.

For the determination of the solubility of black HgS the following method was used. The saturated solutions of cinnabar were diluted to a definite degree and the resulting solutions shaken with the precipitated black HgS till equilibrium was established. The method of analysis was the same as in the case of the cinnabar solutions.

That red HgS is the more stable modification* is proved by (1) the greater solubility of the black variety (Table I., column 4), (2) the fact that on dilution or on treatment with H_2S the black form is precipitated, and (3) the frequently observed transformation of the black to the red variety on standing in contact with the solution. The velocity of this transformation decreases very rapidly with diminishing concentration of the Na_2S solution. In one case with a 2-mol. N solution the transformation was complete in about a day, although a somewhat longer time is usually required. With dilute solutions the red HgS does not appear until after weeks, or even months.

TABLE I.

Conc, Na_2S. Mole/litre.	HgS (red) dissolved. Mole/litre.	Ratio HgS (red) to Na_2S.	HgS (black) dissolved. Mole/litre.	Ratio HgS (black) to Hgs (red).
2·030	1·144	0·5635	—	—
1·52	0·7832	0·5153	0·8561	1·09
1·015	0·4423	0·4328	0·5002	1·13
0·755	0·2878	0·3812	0·3336	1·16
0·50	0·1500	0·3006	0·1805	1·20
0·25	0·04544	0·1818	0·05622	1·24
0·10	0·008241	0·0824	0·01085	1·32

The increase in the ratio of the solubilities of black and red HgS (see Table I., column 5) might be explained by the difference in solubility of the large and small grains of the amorphous black modification,† by assuming

* *Cf.* also Ostwald, *Principles of Inorg. Chemistry*, Eng. trans., p. 666.
† Ostwald, *Zeitschr. f. physik. Chemie*, 1900, **34**, 495.

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that in the dilute solutions of black HgS the small grains, and in the more concentrated solutions the relatively less soluble large grains determine the solubility. In the saturated dilute solutions the small grains would still be left as a solid phase, while in the saturated concentrated solutions the solid phase would consist of large grains only, the more soluble small grains having been dissolved out first. A more probable explanation is, however, the following. On account of the greater velocity of the transformation of black to red in the more concentrated solutions, and the smaller solubility of the latter form, a partial transformation to the red form takes place. The solution is now super-saturated with respect to red HgS, which separates out, so that the maximum solubility of the black modification is not reached. On this assumption the solubility of black HgS does not represent a true equilibrium. Possibly the result is due to a combination of these two causes.

The influence of temperature on the solubility is of interest. The solubility diminishes with increase of temperature, but the temperature coefficient is small.

TABLE II.

Solubility of Cinnabar at 33°.

Conc. of Na_2S. Mole/litre.	Cinnabar dissolved in Mole/litre at	
	33°.	25°.
0·755	0·2828	0·2878
0·50	0·1465	0·1500
0·25	0·04360	0·04544
0·10	0·007887	0·00824

This result is probably due to the simultaneous operation of three different influences—(1) an increasing solubility of HgS, (2) a decrease of the complex-constant, the complex being less stable at higher temperatures, and (3) an increasing hydrolysis, which diminishes the concentration of the sulphur ions. From equation (1) it is evident that the first influence causes an increase in the solubility by increasing the active mass of the HgS, while the two other influences cause a lowering of the solubility.

The hydrolysis of Na_2S takes place according to the equation—

$$Na_2S + H_2O \rightleftarrows NaHS + NaOH,$$

or, expressing the reaction as taking place between the ions only—

$$S'' + H_2O \rightleftarrows HS' + OH'.$$

Applying the law of mass-action, we obtain—

$$\frac{[HS'][OH']}{[S'']} = k_1.$$

k_1 is the hydrolysis-constant. From this equation it is evident that by increasing the concentration of the OH'-ions the hydrolysis will be diminished, *i.e.*, the concentration of the S''-ions will be increased. Since the solubility of HgS in Na_2S depends on the concentration of the S''-ions (see equation (1)) this solubility should be increased by the addition of NaOH to the Na_2S. This conclusion also is confirmed by the experimental results. The following table shows the influence of NaOH of various concentrations on the solubility.

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TABLE III.

Conc. of Na_2S Mole/Litre.	HgS (Red) dissolved in Mole/Litre.						Ratio HgS/Na_2S in the Solutions, with Addition of 7·7N NaOH.
	In Pure Na_2S.	With Addition of 0·5N NaOH.	With Addition of 1·0N NaOH.	With Addition of 4·48N NaOH.	With Addition of 4·67N NaOH.	With Addition of 7·7N NaOH.	
1·015	0·4423	—	0·673	—	—	0·9167	0·903
0·755	0·2878	—	0·485	—	—	—	—
0·50	0·1500	0·2483	0·302	0·435	—	0·4637	0·927
0·25	0·04544	0·1106	0·148	—	0·225	0·2369	0·948
0·10	0·008241	0·03962	0·0563	—	0·0903	0·09634	0·963

The fact that, by the addition of very strong NaOH, which reduces the hydrolysis to a minimum, the dissolved HgS becomes practically equivalent to the Na_2S, indicates that the formula of the complex is Na_2HgS_2, or that of the complex anion HgS_2''.

The following simple experiment demonstrates several of the points treated above. A saturated solution of cinnabar in Na_2S is prepared. H_2S is passed into this solution, when *black* HgS is precipitated. This indicates that black HgS is the unstable modification, and shows that the solubility of HgS in NaHS is very slight compared with that in Na_2S. On adding solid NaOH to the solution the whole of the HgS is brought into solution, and an additional quantity of HgS may be dissolved, illustrating the effect of excess of OH'-ions on the solubility.

B. *Electromotive Force Measurements.*—In the method of Bodländer* we have a means of determining the constitution of complexes. In the present case, however, owing to the difficulty of determining the concentration of the S''-ions, the method is only partially applicable. Its application in the present instance may be summarised as follows.

For the complex anion the mass-action equation—

$$[(Hg)_m(S'')_{m+n}] = k_2[Hg^{\cdot\cdot}]^m[S'']^{m+n}$$

must be fulfilled. Consequently for two solutions which have different values for $[(Hg)_m(S'')_{m+n}]$ but equal values for $[S'']$, we get—

$$[(Hg)_m(S'')_{m+n}]_1 = k_2[Hg^{\cdot\cdot}]_1^m[S'']^{m+n}$$

and—

$$[(Hg)_m(S'')_{m+n}]_2 = k_2[Hg^{\cdot\cdot}]_2^m[S'']^{m+n},$$

and by division—

$$\frac{[(Hg)_m(S'')_{m+n}]_1}{[(Hg)_m(S'')_{m+n}]_2} = \frac{[Hg^{\cdot\cdot}]_1}{[Hg^{\cdot\cdot}]_2^m}.$$

This condition is approximately fulfilled by dissolving small but different quantities of HgS in solutions of Na_2S of the same strength. The amount of S''-ions used up in the complex-formation is then negligible when compared with the total S''-ions in the solution. The ratio $\frac{[Hg^{\cdot\cdot}]_1}{[Hg^{\cdot\cdot}]_2}$ is found by a measurement of the E.M.F. of a concentration-cell composed of the two solutions.

* *Festschrift zum 70 Geburtstage von Dedekind*, Braunschweig, 1901; also *Zeitschr. f. physik. Chemie*, 1902, **39**, 307.

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If E_{25} denote the E.M.F. of such a cell at 25°, the temperature at which all the E.M.F. measurements were made, then, by Nernst's formula—

$$E_{25} = 0{\cdot}0295 \log \frac{[Hg^{\cdot\cdot}]_1}{[Hg^{\cdot\cdot}]_2} = \frac{0{\cdot}0295}{m} \log \frac{[(Hg)_m(S'')_{m+n}]_1}{[(Hg)_m(S'')_{m+n}]_2}.$$

The ratio $\frac{[(Hg)_m(S'')_{m+n}]_1}{[(Hg)_m(S'')_{m+n}]_2}$ is that of the dissolved HgS in the two solutions, since the amount of free HgS must be even less than the saturation concentration (HgS is one of the most insoluble substances), and since the dissociation of the complex anion is negligible when compared with its total concentration. These considerations apply in an even more marked degree to the saturated HgS solutions, so that we are justified in that case also in taking the concentration of the complex as that of the dissolved HgS.

The E.M.F. of a cell in which the above ratio was 2 : 1 was found to be 0·011 volt—

$$0{\cdot}011 = \frac{0{\cdot}0295}{m} \log 2, \therefore m = 0{\cdot}8.$$

m must, of course, be a whole number. It is therefore evident that its value is 1. The error, which corresponds to only 2 millivolts, is probably due to the diffusion potential.

In a similar manner the value of n might be found if we could determine the concentration of the S''-ions. As this is not the case, it is simplest to assume that n is also 1, and that the complex has the formula Na_2HgS_2, as the solubility experiments seem to indicate. The mass-action equation for the dissociation of the complex anion then becomes—

$$[HgS_2''] = K[HgS][S''] = k_3[S''],$$

since the concentration of HgS, as solid phase, is constant.

For the ionic dissociation of HgS the mass-action equation is—

$$[HgS] = k_4[Hg^{\cdot\cdot}][S''],$$

where k_4 is the dissociation constant of HgS, or, since [HgS] is constant—

$$[S''] = \frac{k_5}{[Hg^{\cdot\cdot}]}.$$

Substituting this value of [S''] in the first equation, we obtain—

$$[HgS_2''] = \frac{k_3k_5}{[Hg^{\cdot\cdot}]} = \frac{k_6}{[Hg^{\cdot\cdot}]},$$

i.e., for saturated solutions the product $[HgS_2'']\,[Hg^{\cdot\cdot}]$ is constant.

The concentration of Hg''-ions was determined by measuring the E.M.F. of the solution against a mercury electrode. The calomel normal electrode, in which the Hg''-ion concentration* is 3×10^{-20}, was used as standard electrode. The compensation method was used in the E.M.F. measurements, a capillary electrometer or sensitive galvanometer serving as null-instrument and a Weston element as standard cell.

By applying Nernst's formula—

$$E_{25} = 0{\cdot}0295 \log \frac{3 \times 10^{-20}}{x}$$

we can calculate x, the Hg''-ion concentration in the solution in question.

* Ley and Heimbucher, *Zeitschr. f. Elektrochemie*, 1904, 10, 310.

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The concentration of HgS_2'' has been taken as that of the dissolved HgS (see above).

Table IV. contains the results of these measurements.

TABLE IV.

Conc. of Na_2S Mole/litre.	Conc. of HgS_2'' = Dissolved HgS Mole/litre.	E.M.F. against Calomel Electrode, Volt.	Conc. of Hg'' Gm.-ion/litre.	$[Hg''][HgS_2'']$ $= k_6$.
2·030	1·144	0·9715	$3·53 \times 10^{-53}$	$4·0 \times 10^{-53}$
1·52	0·7832	0·9650	$5·21 \times 10^{-53}$	$4·1 \times 10^{-53}$
1·015	0·4423	0·9570	$10·9 \times 10^{-53}$	$4·8 \times 10^{-53}$
0·755	0·2878	0·9515	$16·5 \times 10^{-53}$	$4·7 \times 10^{-53}$
0·50	0·1500	0·9455	$26·7 \times 10^{-53}$	$4·0 \times 10^{-53}$
0·25	0·04544	0·9335	$58·5 \times 10^{-53}$	$2·7 \times 10^{-53}$
0·10	0·008241	0·9145	300×10^{-53}	$2·5 \times 10^{-53}$

The E.M.F.'s were reproducible to within a millivolt. The diffusion potentials at the point of contact of the two electrolytes have not been taken into account. There is no satisfactory method, applicable to the present case, of getting rid of these diffusion potentials.

In view of this fact and of the extraordinarily small concentration of the Hg''-ions, the constancy of the expression $[Hg''][HgS_2'']$ is very satisfactory, and is a further proof of the correctness of the formula Na_2HgS_2 for the complex.

From the hydrolysis equilibrium for Na_2S—

$$[OH'][HS'] = k_1[S'']$$

we get the relation—

$$[HS']^2 = k_1[S''],$$

since when no excess of NaOH or H_2S is added HS' and OH' are present in equivalent quantities. Further, if we assume complete dissociation—

$$[HS'] + [S''] = a - b,$$

where a is the total concentration of the Na_2S and b that of the dissolved HgS, *i.e.*, of the complex salt.

From these two equations we find—

$$[HS'] = -\frac{k_1}{2} + \sqrt{\left(\frac{k_1}{2}\right)^2 + k_1(a-b)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and $[S''] = a - b - [HS']$, if k_1 be known.

By substituting the values of $[S'']$ so found in the equations—

$$\frac{[HgS_2'']}{[Hg''][S'']^2} = k_2,$$

and—

$$[Hg''][S''] = L$$

we can calculate k_2, the constant for the formation of the complex HgS_2'' from the ions Hg'' and S'', and L, the solubility-product of HgS.

k_1 is the hydrolysis-constant of Na_2S. Its value, calculated from Küster's measurements, is 0·274. This value was used to calculate k_2 and L. The results, however, were so unsatisfactory as to lead to the conclusion that the method of Koelichen and Küster, which gave this value, must be untrust-

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worthy. The method depends on the catalysis of the decomposition of *diacetonealcohol* into 2 molecules of acetone by OH'-ions. I have repeated some of the measurements, and the results, although not very satisfactory, point to a higher degree of hydrolysis than that given by Küster. A discussion of this question will be found in Section II.

I therefore tried different values of k_1 in equation (2) and obtain the best constancy of k_2 and L with values of k_1 between 5 and 10. This indicates a hydrolysis of Na_2S in 0·05 mol. N solution of about 99 per cent., whereas Küster found 86·4 per cent. The order of magnitude of the two numbers is, however, the same. Schaeffer's measurements* (see Section II) also point to a greater degree of hydrolysis than 86 per cent. The results of these calculations are shown in Table V.

TABLE V.

Conc. Na_2S. Mole/Litre.	Conc. S'' $\frac{\text{gm. ion}}{\text{Litre.}}$	$[Hg^{\cdot\cdot}][S''] = L.$	$\frac{[HgS_2'']}{[Hg^{\cdot\cdot}][S'']^2} = k_2$
$k_1 = 0{\cdot}405$. Hydrolysis in 0·05 mol. N solution = 90 per cent.			
2·03	0·456	$1{\cdot}6 \times 10^{-53}$	$1{\cdot}6 \times 10^{53}$
1·52	0·356	$1{\cdot}8 \times 10^{-53}$	$1{\cdot}2 \times 10^{53}$
1·015	0·252	$2{\cdot}7 \times 10^{-53}$	$0{\cdot}64 \times 10^{53}$
0·755	0·189	$3{\cdot}1 \times 10^{-53}$	$0{\cdot}49 \times 10^{53}$
0·50	0·125	$3{\cdot}3 \times 10^{-53}$	$0{\cdot}36 \times 10^{53}$
0·25	0·0549	$3{\cdot}2 \times 10^{-53}$	$0{\cdot}25 \times 10^{53}$
0·10	0·0145	$4{\cdot}4 \times 10^{-53}$	$0{\cdot}13 \times 10^{53}$
$k_1 = 1{\cdot}0$. Hydrolysis in 0·05 mol. N solution = 95 per cent.			
2·03	0·320	$1{\cdot}1 \times 10^{-53}$	$3{\cdot}2 \times 10^{53}$
1·52	0·243	$1{\cdot}3 \times 10^{-53}$	$2{\cdot}6 \times 10^{53}$
1·015	0·166	$1{\cdot}8 \times 10^{-53}$	$1{\cdot}5 \times 10^{58}$
0·755	0·120	$2{\cdot}0 \times 10^{-53}$	$1{\cdot}2 \times 10^{53}$
0·50	0·075	$2{\cdot}0 \times 10^{-53}$	$0{\cdot}99 \times 10^{53}$
0·25	0·0402	$2{\cdot}4 \times 10^{-53}$	$0{\cdot}48 \times 10^{53}$
0·10	0·0072	$2{\cdot}2 \times 10^{-53}$	$0{\cdot}53 \times 10^{53}$
$k_1 = 5$. Hydrolysis in 0·05 mol. N. solution = 99 per cent.			
2·03	0·118	$0{\cdot}42 \times 10^{-53}$	23×10^{53}
1·52	0·0848	$0{\cdot}44 \times 10^{-53}$	21×10^{53}
1·015	0·0537	$0{\cdot}58 \times 10^{-53}$	14×10^{53}
0·755	0·0372	$0{\cdot}61 \times 10^{-53}$	13×10^{53}
0·50	0·0217	$0{\cdot}58 \times 10^{-53}$	12×10^{53}
0·25	0·0076	$0{\cdot}44 \times 10^{-53}$	13×10^{53}
0·10	0·00176	$0{\cdot}53 \times 10^{-53}$	9×10^{53}
$k_1 = 10$. Hydrolysis in 0·05 mol. N solution = 99·5 per cent.			
2·03	0·067	$0{\cdot}24 \times 10^{-53}$	$7{\cdot}2 \times 10^{54}$
1·52	0·048	$0{\cdot}25 \times 10^{-53}$	$6{\cdot}5 \times 10^{54}$
1·015	0·030	$0{\cdot}33 \times 10^{-53}$	$4{\cdot}5 \times 10^{54}$
0·755	0·022	$0{\cdot}36 \times 10^{-53}$	$3{\cdot}6 \times 10^{54}$
0·50	0·011	$0{\cdot}29 \times 10^{-53}$	$4{\cdot}6 \times 10^{54}$
0·25	0·0041	$0{\cdot}24 \times 10^{-53}$	$4{\cdot}6 \times 10^{54}$
0·10	0·00076	$0{\cdot}23 \times 10^{-53}$	$4{\cdot}8 \times 10^{54}$

* Dissertation, Leipzig.

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The uncertainty of the values of the S″-ion concentrations, which occur as a square in the expression for k_2, and the influence of the diffusion-potentials, are sufficient to explain the variation of k_2.

There can be no doubt that the order of magnitude of the constants is correct, and the assumption of the formula Na_2HgS_2 for the complex may be regarded as proved.

It may be pointed out here that what has been proved is only that HgS_2'' is the *predominating* complex within the limits of concentration investigated. The existence of other complexes is not excluded. Analogy with K_2S, which forms various solid complex compounds with HgS,* makes it probable that complexes other than HgS_2'' also exist in Na_2S solutions, though in small amount compared with the latter. Further, it does not follow that since Na_2HgS_2 is the predominating complex, it should separate out as a solid phase on concentrating the solution. That complex will separate out first whose solubility-product is first reached. Numerous instances are known in which a certain type of complex predominates in solution, while the solid complexes which have been isolated from the solution have a different composition.†

When a solution saturated with both HgS and Na_2S is concentrated *in vacuo* over sulphuric acid, a crystalline solid is deposited in yellow leaflets, along with crystals of Na_2S. The mother-liquor was poured off and the mixture of crystals dried *in vacuo* over sulphuric acid. The Na_2S was removed as far as possible by allowing the solid to stand under absolute alcohol, which was frequently renewed. The yellow compound was then filtered into a Neubauer platinum crucible, washed with absolute alcohol and dried *in vacuo* over sulphuric acid. The compound thus obtained is bright yellow.

For analysis a weighed quantity was decomposed by HCl or H_2SO_4, sulphuretted hydrogen passed in, and the HgS collected in a Gooch's crucible and weighed. The Na_2S was determined as NaCl or Na_2SO_4 by evaporating the filtrate to dryness.

On heating the compound in a dry test-tube water was given off, so that it evidently contains water of crystallisation. The water of crystallisation was determined by heating a weighed quantity of the compound to 100°–105° in an atmosphere of hydrogen till the weight was constant. The substance left after expelling the water of crystallisation was brownish-black.

The analytical figures are as follows—

	Found.		Calculated for
	I.	II.	$2Na_2S.5HgS.3H_2O$.
Na_2S	10·93 per cent.	11·25 per cent.	11·39 per cent.
HgS	84·94 „	84·51 „	84·67 „
H_2O	4·30 „	4·22 „	3·94 „

In I. the Na_2S was determined as NaCl, in II. as Na_2SO_4. In another experiment the ratio of the number of molecules of HgS to Na_2S was determined in a sample of the compound which had slightly decomposed on exposure to air. This, however, does not affect the result. The ratio found was $HgS/Na_2S = 5{\cdot}06/2$, instead of the theoretical 5/2.

The formula of the double sulphide of sodium and mercury is, therefore, $2Na_2S.5HgS.3H_2O$. In this case too, then, the solid compound which separates out has a composition different from that of the complex predominating in the solutions investigated above.

* Dammer, Handbuch, vol. ii. Part II, p. 885.

† See, for example, Hamburger and Abegg, *Zeitschr. f. anorg. Chemie*, 59, 405. Also Sherrill, *Zeitschr. f. physik. Chemie*, 43, 705.

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Solubility of HgS in K_2S and in BaS Solutions.—From the general analogy between sodium and potassium salts it was to be expected that the constitution of K_2S solutions would be similar to that of Na_2S solutions, and therefore that the solubility of HgS in K_2S would be approximately the same as in Na_2S. In view, however, of the conflicting statements given in Dammer's Handbuch* regarding the solubility of HgS in alkali sulphides, it was considered advisable to determine the solubility in K_2S, and its variation with concentration. The K_2S solutions were prepared from potassium hydroxide (crystallised from alcohol), from which the carbonate was precipitated by the addition of barium hydroxide. The determinations were carried out in the same manner as for Na_2S solutions. The results, contained in Table VI., show that the solubility of HgS in K_2S solutions is somewhat greater than in the corresponding Na_2S solutions, and are, therefore, quite normal, the greater solubility being in accord with the greater electro-affinity of potassium compared with sodium.

TABLE VI.

Conc. K_2S. Mole/litre.	HgS (red) dissolved. Mole/litre.	HgS (black) dissolved. Mole/litre.	Ratio HgS (black) to HgS (red.
1·0	0·4629	—	—
0·5	0·1588	0·1836	1·16
0·25	0·04839	0·06000	1·24

The addition of KOH or NaOH to the K_2S causes a large increase in the solubility of HgS, and on adding a very strong solution of KOH the HgS dissolved becomes practically equivalent to the K_2S. The behaviour of K_2S solutions towards HgS is, therefore, perfectly analogous to that of Na_2S solutions, so that we may conclude that the same complex anion, HgS_2'', exists in both. Table VII. shows the effect of the addition of KOH and NaOH on the solubility of HgS in K_2S. KOH causes a greater increase in the solubility than the same strength of NaOH. The effect of the addition of an electrolyte with a common ion in putting back the dissociation of K_2S is evidently more than counterbalanced by the greater hydrolysis of Na_2S.

TABLE VII.

Conc. K_2S Mole/litre.	Conc. KOH Added.	Conc. NaOH Added.	HgS (red) dissolved Mole/litre.
0·25	1 N	—	0·1616
0·25	0·5 N	—	0·1189
0·25	6·35 N	—	0·2399
0·25	—	1 N	0·1583
0·25	—	0·5 N	0·1163

The solubility of HgS in 0·1 mol. N BaS was found to be 0·008241 mole/litre, practically the same as in the corresponding strength of Na_2S.

C. *The Solubility of Cinnabar in Na_2S_2 Solutions.*—The Na_2S_2 solutions were prepared by dissolving the requisite quantity of sulphur (crystallised from

* Vol. ii. (2), pp. 881, 885, 886.

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carbon disulphide) in Na_2S solutions. To determine the amount of HgS dissolved a definite volume of the solution was pipetted out, after equilibrium had been established, and acidified with hydrochloric acid. The HgS was precipitated together with the excess of sulphur. Sulphuretted hydrogen was passed in for a short time and the precipitate collected in a Gooch's crucible, washed with alcohol and carbon disulphide, dried, and weighed. The extraction with carbon disulphide was repeated until the weight was constant.

In polysulphide solutions the complex sulphur anions S_2'', S_3'', S_4'', &c., are present in equilibrium with one another. It is to this complex formation that the solubility of sulphur in Na_2S is due. Thus—

$$S + S'' \rightleftarrows S_2'', \text{ \&c.}$$

The process is analogous to the complex-formation between HgS and S'', $HgS + S'' \rightleftarrows HgS_2''$.

When HgS is dissolved in Na_2S_2 solutions the S''-ions will be distributed between the competing HgS and S in a ratio depending on the stability of the various complexes, or in other words, on the affinity of the various "neutral parts" for the "simple ion." It is quite possible, therefore, that in spite of the smaller degree of hydrolysis of Na_2S_2 compared with Na_2S,* the solubility of HgS will be less in the disulphide than in the monosulphide. The experimental results contained in Table VIII. show that the solubility in Na_2S is approximately double that in the corresponding Na_2S_2 solutions :—

TABLE VIII.

Conc. Na_2S_2. Mole/litre.	HgS dissolved. Mole/litre.	Ratio. HgS/Na_2S_2.	Ratio. $\frac{\text{HgS in } Na_2S}{\text{HgS in } Na_2S_2}$
2·0	0·6043	0·3026	1·89
1·5	0·4130	0·2753	1·89
1·0	0·2339	0·2339	1·89
0·75	0·1504	0·2005	1·91
0·50	0·07598	0·1519	1·97
0·25	0·02238	0·08952	2·03
0·10	0·003859	0·03859	2·13

The influence of NaOH on the solubility is here also very marked, but the ratio HgS : Na_2S_2 is much less than the corresponding ratio in the monosulphide solutions.

TABLE IX.

Influence of NaOH on the Solubility of Cinnabar in Na_2S_2.

Conc. Na_2S_2 Mole/litre.	Conc. NaOH Mole/litre.	HgS Dissolved Mole/litre.	Ratio HgS/Na_2S_2.
0·25	4·33	0·1378	0·5512
0·10	5·0	0·05602	0·5602

* Küster and Heberlein, *Zeitschr. f. anorg. Chemie*, 43, 71.

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Electromotive measurements were also undertaken with these solutions. The potentials, however, were not so well defined as in the case of the monosulphide solutions.

If the same complex anion HgS_2'' is formed in the disulphide solutions as in the monosulphide, the product $[HgS_2''][Hg^{\cdot\cdot}]$ should be a constant and equal to k_6, since exactly the same reasoning for deducing the equation is applicable in this case.

As will be seen from Table X., which contains the E.M.F. measurements, the expression $[HgS_2''][Hg^{\cdot\cdot}]$ is approximately constant, and the constant is of the same order of magnitude as k_6 for the monosulphide solutions. The divergence is due partly to the smaller degree of accuracy attained in the E.M.F. measurements, but it is also possible that HgS_2'' is not the only complex formed in this case, or rather that it does not predominate to such a large extent, since even in the monosulphide solutions it is probable that complexes other than HgS_2'' are present, though in relatively small amounts.

TABLE X.

Conc. Na_2S_2 Mole/litre.	Conc. HgS_2'' Mole/litre.	E.M.F. against Calomel Electrode Volt.	Conc. $Hg^{\cdot\cdot}$ Gm. Ion/litre.	$[HgS_2''][Hg^{\cdot\cdot}]$.
2·0	0·6043	0·957	$1·09 \times 10^{-52}$	$6·6 \times 10^{-53}$
1·5	0·4130	0·949	$2·02 \times 10^{-52}$	$8·4 \times 10^{-53}$
1·0	0·2339	0·937	$5·18 \times 10^{-52}$	$12·1 \times 10^{-53}$
0·75	0·1504	0·935	$6·05 \times 10^{-52}$	$9·1 \times 10^{-53}$
0·5	0·07598	0·922	$16·7 \times 10^{-52}$	$12·7 \times 10^{-53}$
0·25	0·02238	0·909	46×10^{-52}	$10·3 \times 10^{-53}$
0·10	0·003859	0·882	378×10^{-52}	$14·6 \times 10^{-53}$

II. THE HYDROLYSIS OF Na_2S SOLUTIONS.

The hydrolysis of Na_2S was measured by Küster by Koelichen's method,* which consists in measuring the rate at which diacetone alcohol is split up into acetone under the catalytic influence of hydroxyl ions. The reaction, which is accompanied by a considerable increase in the volume of the reaction mixture, is allowed to take place in a dilatometer, and from the observed expansion the velocity constant k is calculated by the formula for a monomolecular reaction—

$$k = \frac{1}{t - t_o} \log \frac{a - x_o}{a - x_t},$$

in which t denotes the time of reading, t_o the time of the first reading $a - x_o$ the dilatation from the time t_o to the end of the reaction, and $a - x_t$ the dilatation from the time t till the end; $a - x_o$ and $a - x_t$ are proportional to the quantities of diacetone alcohol present at the respective times of reading.

Koelichen assumes proportionality between the velocity-constants and the concentration of OH'-ions, and takes the constant for a mixture of 20 c.c. of 0·1 N. NaOH and 1·0526 gm. diacetone alcohol as his standard. The values of k calculated on this assumption agree fairly well with the observed values when the concentration of OH'-ions is not too far from that of the standard. For example, in 0·02 and 0·01 N. solutions of NaOH the calculated and observed values agree within about 4½ per cent. while in 0·005 N solution the

* *Zeitschr. f. physik. Chemie*, 33, 129.

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divergence is nearly 11 per cent. In all these measurements both Koelichen and Küster used a mixture of 1·0526 gm. diacetone alcohol, and 20 c.c. of the alkaline solution, and I have used the same proportions in the experiments given below.

For the mixture with 0·1 N. NaOH Koelichen found the velocity-constant 0·02181. The titre of the solution was 0·0942, and from Ostwald's tables the degree of dissociation $\frac{\mu_v}{\mu_\infty}$ was found to be 0·92. The concentration of OH′-ions was, therefore, 0·08762.

Küster uses these results to calculate the hydrolysis of Na_2S as follows. The velocity-constant in 0·05 mol. N. Na_2S solution was found to be 0·00985. The concentration of OH′-ions is therefore $0{\cdot}00985 \times \frac{0{\cdot}08762}{0{\cdot}02181} = 0{\cdot}0396$. From this he calculates that the total concentration of NaOH (dissociated and undissociated) would be 0·0412 if no other substance were present, *i.e.*, the concentration of undissociated NaOH would be 0·0016. But the hydrolysis furnishes NaHS also (its concentration is taken as 0·0588 approximately), and, assuming this to be about 86 per cent. dissociated, the concentration of $Na^{\cdot}$-ions furnished by its dissociation is 0·0506 N. The total concentration of $Na^{\cdot}$-ions is therefore $0{\cdot}0396 + 0{\cdot}0506 = 0{\cdot}0902$. This excess of $Na^{\cdot}$-ions puts back the dissociation of NaOH, so that the concentration of undissociated NaOH is greater than 0·0016, which corresponds to a $Na^{\cdot}$-ion concentration of only 0·0396. Küster therefore takes the concentration of undissociated NaOH as $0{\cdot}0016 \times \frac{0{\cdot}0902}{0{\cdot}0396} = 0{\cdot}0036$, and the total concentration of NaOH, dissociated and undissociated, as $0{\cdot}0036 + 0{\cdot}0396 = 0{\cdot}0432$. Accordingly the 0·05 mol. N Na_2S solution is $100 \times \frac{0{\cdot}0432}{0{\cdot}0500} = 86{\cdot}4$ per cent hydrolysed. The hydrolysis constant is therefore—

$$k_1 = \frac{(0{\cdot}0432)^2}{0{\cdot}0068} = 0{\cdot}274.$$

Küster's method of calculation is open to the objection that we are here dealing with a mixture of practically equally strong electrolytes. In such a mixture it may be shown * that the degree of dissociation is the same for all, and equal to that in a solution of any one of them, whose concentration is equal to the total concentration of the mixture.

It is more rational, then, to take the degree of dissociation as equal to that in a 0·1 N NaOH solution. From Kohlrausch's tables $\frac{\mu_v}{\mu_\infty} = \frac{183}{218{\cdot}4} = 0{\cdot}838$.† If we accept Küster's figure for the concentration of OH′- ions (0·0396), the total concentration of NaOH will be $\frac{0{\cdot}0396}{0{\cdot}838} = 0{\cdot}04726$, and the hydrolysis 94·5 per cent., or about 8 per cent. higher than that calculated by Küster. The hydrolysis-constant now becomes $k_1 = \frac{(0{\cdot}04796)^2}{0{\cdot}00274} = 0{\cdot}815$. The hydrolysis constant 0·405, used in Table V., would give a hydrolysis of 90 per cent. in 0·05 N solution—a mean of the results of the two methods of calculation.

To get an independent estimate of the degree of hydrolysis the following dilatometric experiments were performed. The results indicate a degree of hydrolysis at the dilutions measured in agreement with that furnished by the

* See, for example, Abegg, *Dissociationstheorie*, p. 50.

† At 18°. At 25°, the temperature at which the experiments were carried out, it will not be much different.

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HgS solubility method. The NaOH was prepared from sodium, and the Na_2S freshly made from this soda. The same diacetone alcohol (B.P. 162°–166°), and the same dilatometer were used in each case, so that the results are strictly comparable.

1·3157 gm. diacetone alcohol + 25 c.c. 0·1 N NaOH.

Time in Mins.	Dilatom. Reading.	$k = \frac{1}{t - t_0} \log \frac{a - x_0}{a - x_t}$
0	1·51	—
1	2·61	0·02004
2	3·65	0·01994
3	4·67	0·02008
4	5·67	0·02030
5	6·61	0·02037
6	7·50	0·02039
7	8·37	0·02049
8	9·18	0·02049
9	9·97	0·02055
10	10·70	0·02053
11	11·42	0·02058
12	12·10	0·02061
13	12·73	0·02058
14	13·36	0·02063
16	14·48	0·02059
18	15·50	0·02051
20	16·43	0·02054
22	17·30	0·02057
24	18·01	0·02042
26	18·70	0·02038
∞	25·90	mean = 0·02043

1·3157 gm. diacetone alcohol + 25 c.c. 0·1 mol. N Na_2S.

Time in Mins.	Dilatom. Reading.	$k = \frac{1}{t - t_0} \log \frac{a - x_0}{a - x_t}$
0	0·73	—
1	1·57	0·02027
2	2·33	0·01973
3	3·09	0·01985
4	3·80	0·01979
5	4·53	0·02007
6	5·22	0·02022
7	5·88	0·02034
8	6·48	0·02031
9	7·06	0·02032
10	7·59	0·02023
11	8·11	0·02021
12	8·62	0·02024
13	9·09	0·02020
14	9·54	0·02017
16	10·40	0·02020
18	11·14	0·02009
20	11·81	0·01998
∞	19·15	mean = 0·02013

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1·3157 gm. diacetone alcohol + 25 c.c. 0·05 mol. N Na_2S.

Time in Mins.	Dilatom. Reading.	$k = t\frac{1}{t - t_0} \log \frac{a - x_0}{a - x_t}$
0	0·00	—
1	0·75	0·01009
2	1·48	0·01007
3	2·17	0·00996
4	2·87	0·00999
5	3·54	0·00997
6	4·22	0·01002
7	4·86	0·01000
8	5·52	0·01006
9	6·15	0·01007
10	6·72	0·01008
11	7·37	0·01010
12	7·96	0·01011
13	8·55	0·01014
14	9·10	0·01013
16	10·20	0·01016
18	11·23	0·01019
20	12·23	0·01019
∞	32·65	mean = 0·01008

If we take the concentration of OH′-ions in 0·1 N NaOH as 0·0838, then in 0·1 mol. N Na_2S it will be $\frac{0·02013}{0·02043} \times 0·0838 = 0·08257$, and the concentration of NaOH (dissociated + undissociated) $= \frac{0·08257}{0·815} = 0·101$; 0·815 is the degree of dissociation in 0·2 N. NaOH. According to this result the hydrolysis is complete.

Similarly, for the 0·05 mol. N. Na_2S solution—

$$OH'\text{-conc.} = \frac{0·01008}{0·02043} \times 0·0838 = 0·04133.$$

$$\text{Total NaOH conc.} = \frac{0·04133}{0·838} = 0·04934.$$

Hydrolysis = 98·7 per cent.

The hydrolysis found in 0·05 mol. N. solution is probably nearer the truth than that found in 0·1 mol. N. solution, since in the former case the influence of the neutral salt (see below) is much less. The fact that the constant for 0·05 Na_2S is half that for 0·1 Na_2S shows that the hydrolysis is practically complete.

There are several reasons for regarding the results obtained by the diacetone alcohol method as approximations only.

(1) The degree of dissociation of NaOH is not known with any degree of certainty, since the mobility of the ions at infinite dilution, and especially of OH′-ions, can be determined only approximately. In a case like the present, where the concentration of Na_2S, which is small, is found by taking the difference of two large numbers (total concentration — NaOH concentration), a small error in the NaOH concentration will affect the hydrolysis-constant enormously, since $k_1 = \frac{(\text{conc. NaOH})^2}{\text{conc. } Na_2S}$. If, for example, in calculating the total concentration of NaOH in 0·05 N Na_2S from Küster's figure for

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the OH′-ion concentration (0·0396), we use 0·88 as the degree of dissociation instead of 0·838, we get the hydrolysis-constant 0·405 instead of 0·815.

(2) Koelichen showed in his original paper that neutral salts have a strong individual influence on the velocity-constant. The constant for 0·1 N. NaOH, for example, is lowered 22·4 per cent. by the addition of N. NaCl, 28·5 per cent. by N. $NaNO_3$, and 4·7 per cent. by N. $Na_2S_2O_3$, while it is raised 4·9 per cent. by the addition of N. Na_2SO_4.

In the Na_2S solutions the NaOH is accompanied by an equivalent amount of NaHS, and the effect of this on the velocity-constant cannot be taken into account, though it may be of the order of magnitude indicated above.

(3) The unpleasant smell, perceived on mixing diacetone alcohol with Na_2S solutions, points to the formation of a new compound. This, however, does not apparently affect the result, since the values of k remain constant throughout the experiment.

The approximate hydrolysis of Na_2S may also be calculated from Schaeffer's measurements of the conductivity of NaOH, NaHS, and a mixture of the two.

The specific conductivity of 0·05917 N. NaOH was $11·61 \times 10^{-3}$ reciprocal ohms, of 0·05917 N. NaHS, the hydrolysis of which was reduced as far as possible by passing in H_2S, $5·50 \times 10^{-3}$ reciprocal ohms, and of a mixture which was 0·05917 N. for both NaOH and NaHS, $16·44 \times 10^{-3}$ reciprocal ohms. If Na_2S were completely hydrolysed, the conductivity of the mixture would be $17·11 \times 10^{-3}$ reciprocal ohms. Let x be the fraction hydrolysed, then $(1 - x)$ is the amount of Na_2S, whose conductivity may be taken as equal to that of NaHS. Then—

$$16·44 = x(17·11) + (1 - x)5·50$$

and $x = 0·94$ or the hydrolysis is 94 per cent. in 0·05917 mol. N. solution.

The method is not an accurate one, but it indicates a higher degree of hydrolysis than that found by Küster.

From the considerations put forward in this section it is evident that no method depending on the measurement of the OH′-ion concentration can give more than an approximate estimate of the degree of hydrolysis of Na_2S. In the absence of an accurate direct method of determining the concentration of S″-ions, the HgS solubility method gives the surest criterion of the degree of hydrolysis, as it depends only on the fulfilment of the law of mass-action for the reaction—

$$Hg^{\cdot\cdot} + 2S'' = HgS''_2.$$

This has been proved in so many similar cases, that it is safe to assume it here too.

III. The Constitution of some Sulphide Solutions.

A knowledge of the hydrolysis constant k_1 of Na_2S enables us to calculate the second dissociation constant of H_2S.

From the equations—

$$[H^{\cdot}][OH'] = k_w$$

$$\text{and } [HS'][OH'] = k_1[S'']$$

we get—

$$\frac{[H^{\cdot}][S'']}{[HS]} = \frac{k_w}{k_1} = k_{HS'}.$$

k_w is the water-constant and $= 1·2 \times 10^{-14}$. k_1 we may take in round numbers as 10. Substituting these values in the above equation, we obtain—

$$k_{HS'} = \frac{1·2 \times 10^{-14}}{10} = 1·2 \times 10^{-15}$$

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This second dissociation-constant of H_2S enables us further to give the ratio of the concentration of S''- and HS'- ions in all aqueous sulphide solutions at 25°, if the H·- or OH'- titre be known, since—

$$[S''] : [HS'] = \frac{1{\cdot}2 \times 10^{-15}}{[H\cdot]} = 0{\cdot}1\,[OH'].$$

Thus, for example—

in *neutral* solution ($[OH'] = 1{\cdot}1 \times 10^{-7}$)
$[S''] = 1{\cdot}1 \times 10^{-8}\,[HS']$,

in 1N *acid* solution ($[OH'] = 1{\cdot}2 \times 10^{-14}$)
$[S''] = 1{\cdot}2 \times 10^{-15}\,[HS']$,

in 1N *basic* solution ($[OH'] = 1$)
$[S''] = 0{\cdot}1\,[HS']$,

and not until 10-N basic solution ($[OH'] = 10$)
is $[S''] = [HS']$.

The saturation concentration of H_2S in aqueous solution at 25° is very nearly 0·1 N. The first dissociation-constant of H_2S, k_{H_2S}, is according to Auerbach *—

$$k_{H_2S} = \frac{[HS']\,[H\cdot]}{[H_2S]} = 9{\cdot}1 \times 10^{-8}.$$

Accordingly in this solution, the H·- = HS'- ion concentration is—

$$\sqrt{0{\cdot}1 \times 9{\cdot}1 \times 10^{-8}} = 0{\cdot}95 \times 10^{-4}.$$

Further, from the equation—

$$k_{HS'} = \frac{[H\cdot]\,[S'']}{[HS']} = 1{\cdot}2 \times 10^{-15}\ (\text{at } 25°),$$

it is evident that in all pure aqueous solutions of H_2S, in which $[H\cdot]$ is always practically equal to $[HS']$, the S''- ion concentration has the extraordinarily small value $[S''] = 1{\cdot}2 \times 10^{-15}$. In spite of this minute concentration the S''- ions are able to precipitate the heavy metallic ions from their solutions, on account of the extremely small solubility-products of their sulphides.

The knowledge of these various constants is important for the theory of H_2S precipitations. With their help we can calculate the S''- ion concentrations in sulphide solutions, and hence determine the solubility-products of the "insoluble" sulphides,† as has been done in the present investigation for HgS.

The complex Na_2HgS_2 is the sodium salt of a thio-acid H_2HgS_2. The free acid, or its ions, would be formed by dissolving HgS in H_2S water, the S''- ions of which must combine with the HgS to form a certain amount of HgS_2''- ions.

Now Picton and Linder‡ have shown that under certain circumstances H_2S water is capable of dissolving considerable quantities of HgS, up to about 10 gms. per litre. They prove, however, that the solution is colloidal and that the whole of the HgS may be removed by filtering through a very fine porous cell.

* *Zeitschr. f. physik. Chemie*, 49, 217.

† The similar problem for the O''- ions and the solubility-product of the metallic oxides has not yet been solved.

‡ J. C. S., 61, 114 (1892).

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The solubility of HgS in water saturated with H_2S (at 25°) can be calculated approximately with the aid of the constants already found. The result is a confirmation of the conclusions of Picton and Linder, since the concentration of HgS due to complex-formation in such a solution is of the order of magnitude 10^{-14}.

The method of calculation is as follows:—

By multiplying the equations—

$$L = [Hg^{\cdot\cdot}][S''] = 2{\cdot}8 \times 10^{-54} \text{ and } \frac{[HgS_2'']}{[Hg^{\cdot\cdot}][S'']^2} = 5{\cdot}1 \times 10^{54},$$

we get—

$$\frac{[HgS_2'']}{[S'']} = 14{\cdot}3.$$

But—

$$\frac{[H^{\cdot}][S'']}{[HS']} = 1{\cdot}2 \times 10^{-15},$$

$$\therefore \frac{[HgS_2'']}{[HS']} = \frac{1{\cdot}7 \times 10^{-14}}{[H^{\cdot}]} = 1{\cdot}4[OH'] \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

since—

$$[H^{\cdot}] = \frac{1{\cdot}2 \times 10^{-14}}{[OH']}.$$

From (*a*) it is evident that the concentration of HgS_2'' is negligible when compared with that of $H^{\cdot}$ or HS'. The conditions are, therefore, practically the same as in a saturated aqueous solution of H_2S and $[H^{\cdot}] = [HS']$. Accordingly from (*a*)—

$$[HgS_2''] = 1{\cdot}7 \times 10^{-14}.$$

In conclusion, it is of interest and importance to calculate the concentrations of the S''- and a few other characteristic ions in some of the more important solutions used in sulphide precipitations.

1. Using the hydrolysis-constant $k_z = 10$, we find the degree of hydrolysis in 1 mol. N Na_2S solution to be 91 per cent.* hence $[HS'] = [OH'] = 0{\cdot}91$ mol.; $[S''] = 0{\cdot}09$ mol., if we neglect the degree of dissociation, which does not influence the order of magnitude of the results.

2. The hydrolysis of NaHS solutions takes place according to the equation $NaHS + H_2O = NaOH + H_2S$.

The hydrolysis-constant for NaHS is—

$$\frac{k_w}{k_{H_2S}} = \frac{1{\cdot}2 \times 10^{-14}}{9{\cdot}1 \times 10^{-8}} = 1{\cdot}3 \times 10^{-7}.$$

In a 1 mol. N solution, therefore—

$$[H_2S] = [OH'] = 3{\cdot}6 \times 10^{-4}, \text{ and } [HS'] \text{ is practically} = 1;$$

$$[H^{\cdot}] = \frac{k_w}{[OH']} = \frac{1{\cdot}2 \times 10^{-14}}{3{\cdot}6 \times 10^{-4}} = 3{\cdot}3 \times 10^{-11},$$

and—

$$[S''] = \frac{k_{HS'}}{[H^{\cdot}]} = \frac{1{\cdot}2 \times 10^{-15}}{3{\cdot}3 \times 10^{-11}} = 3{\cdot}6 \times 10^{-5}.$$

3 and 4. The relations between the various ions in ammonium sulphide solutions are most simply treated by considering first the case of a 1 mol. N solution of NH_4HS. The hydrolysis here is according to the equation—

$$NH_4HS + H_2O = NH_4OH + H_2S.$$

* See, for example, Abegg, *Dissociationstheorie*, p. 51.

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Since we are here dealing with a salt of a weak acid and a weak base, the hydrolysis-constant is—

$$\frac{k_w}{k_b \cdot k_{H_2S}} = \frac{1{\cdot}2 \times 10^{-14}}{2{\cdot}3 \times 10^{-5} \times 9{\cdot}1 \times 10^{-8}} = 0{\cdot}57 \times 10^{-2},$$

where k_b is the dissociation-constant of NH_4OH; hence the degree of hydrolysis, which in such a salt is independent of the dilution, is 0·07, or 7 per cent. We get, therefore, approximately $[H_2S] = 0{\cdot}07$; $[HS'] = [NH_4^{\cdot}] = 0{\cdot}93$, and from this, with the aid of the constants k_b, k_w, and $k_{HS'}$—

$$[OH'] = 1{\cdot}7 \times 10^{-6}; \quad [H^{\cdot}] = 0{\cdot}7 \times 10^{-8}; \quad [S''] = 1{\cdot}6 \times 10^{-7}.$$

The $(NH_4)_2S$ solution differs from the NH_4HS in containing an additional molecule of NH_3. The effect of this will be to put back the hydrolysis of NH_4HS practically completely and make $[HS'] = 1$, since even in Na_2S solution, where we are dealing with a strong base, the first stage of the hydrolysis is 0·91, or nearly 1. We may, therefore, put $[HS'] = [NH_4^{\cdot}] =$ ca. 1. The concentration of the remaining ammonia will be also ca. 1, since in the presence of 1 mol. $(NH_4^{\cdot})$ it will be practically undissociated. From k_b we then obtain $[OH'] = 2{\cdot}3 \times 10^{-5}$, and from this with k_w, $[H^{\cdot}] = 5 \times 10^{-10}$. Further, with $k_{HS'}$ and k_{H_2S} we get $[S''] = 2{\cdot}4 \times 10^{-6}$ and $[H_2S] = 5{\cdot}5 \times 10^{-3}$.

5. As calculated above for water saturated with H_2S at 25°—

$$[HS'] = 0{\cdot}95 \times 10^{-4}; \quad [S''] = 1{\cdot}2 \times 10^{-15}; \quad [H^{\cdot}] = 0{\cdot}95 \times 10^{-4}; \quad [H_2S] = 0{\cdot}1.$$

With k_w we find $[OH'] = 1{\cdot}3 \times 10^{-10}$.

6. In 1 N. acetic acid saturated with H_2S, in which the S''-ion concentration still suffices for the precipitation of $Zn^{\cdot\cdot}$-ions, the $[H^{\cdot}]$ concentration is—

$$\sqrt{18 \cdot 10^{-6}} = 4 \times 10^{-3},$$

being the square root of the dissociation constant of acetic acid. Hence—

$$[HS'] = 2{\cdot}1 \times 10^{-6}; \quad [S''] = 0{\cdot}65 \times 10^{-18}; \quad [OH'] = 3 \times 10^{-12}; \quad [H_2S] = 0{\cdot}1.$$

7. In 1 N. hydrochloric acid saturated with H_2S, which still contains sufficient S''-ions for the precipitation of the most difficultly soluble sulphides, the concentration of $H^{\cdot}$-ions = 1; hence, since $[H_2S] = 0{\cdot}1$—

$$[HS'] = 0{\cdot}91 \times 10^{-8}; \quad [S''] = 1{\cdot}1 \times 10^{-23}; \quad [OH'] = 1{\cdot}2 \times 10^{-14}.$$

In all cases the dissociation of the strong electrolytes has been assumed to be complete; this does not affect the order of magnitude of the various concentrations, which are, of course, to be regarded as approximations only

The concentrations calculated above are collected in Table XI.; they may serve as a guide to the concentration-relations obtaining in the precipitation of the sulphides in analysis. They show, further, whether the reaction of the alkali sulphides is acid, neutral, or alkaline. Since in all cases $[OH']$ is greater than $[H^{\cdot}]$, they all react alkaline.*

IV. The Solubility of some Sulphides soluble with difficulty.

By measuring the electromotive force of a metal in a solution of sodium sulphide of known strength, and therefore of known S''-ion concentration, the concentration of the metallic ions in a saturated solution of the metallic

* Compare the statement in Ostwald's *Principles of Inorg. Chem.*, English trans., pp. 268, 269, which is accordingly to be corrected.

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TABLE XI.

No.	Solution.	S''.	HS'.	H_2S.	H'.	OH'.
1.	1 mol. N Na_2S	0·09	0·91	$1·3 \times 10^{-7}$	$1·3 \times 10^{-14}$	0·91
2.	1 mol. N NaHS	$3·6 \times 10^{-5}$	1	$3·6 \times 10^{-4}$	$3·3 \times 10^{-11}$	$3·6 \times 10^{-4}$
3.	1 mol. N $(NH_4)_2S$	$2·4 \times 10^{-6}$	ca. 1	$5·5 \times 10^{-3}$	5×10^{-10}	$2·3 \times 10^{-5}$
4.	1 mol. N NH_4HS	$1·6 \times 10^{-7}$	0·93	0·07	$0·7 \times 10^{-8}$	$1·7 \times 10^{-6}$
5.	Saturated aqueous H_2S	$1·2 \times 10^{-15}$	$0·95 \times 10^{-4}$	0·1	$0·95 \times 10^{-4}$	$1·3 \times 10^{-10}$
6.	Sat. H_2S + 1 N acetic acid	$0·65 \times 10^{-18}$	$2·1 \times 10^{-6}$	0·1	$4·2 \times 10^{-3}$	3×10^{-12}
7.	Sat. H_2S + 1 N HCl	$1·1 \times 10^{-23}$	$0·91 \times 10^{-8}$	0·1	1	$1·2 \times 10^{-14}$

sulphide may be determined, and hence the solubility-product of the sulphide. The metal becomes covered with a layer of sulphide, giving a saturated solution in the neighbourhood of the electrode.

In this manner the solubility products of Ag_2S, PbS, and CuS were determined. The measurements were made in a thermostat at 25° by the compensation method, with a Lippmann electrometer as zero-instrument and a normal calomel electrode as standard electrode. A Weston cadmium cell was used as standard electromotive force. In all cases the connecting vessel between the two half-elements was filled with N. KCl. The sodium sulphide electrode vessels were filled in a current of hydrogen, which was washed by a solution of sodium sulphide of the same strength as that in the electrode vessel. In some cases the hydrogen current was continued during the whole period of measurement; in others the electrode vessel, after being filled with hydrogen, was closed. Oxidation by atmospheric oxygen was thus prevented. For each cell measurements were made at frequent intervals for a period of about six hours, during which time the E.M.F. remained constant. The diffusion-potential at the junction of the two electrolytes has not been taken into account.

Ag_2S.—The electrode was either a pure silver rod or a platinum point electrolytically coated with silver from a solution of potassium silver cyanide. The same result was obtained whether a pure silver electrode was used or one which had been previously covered with a film of sulphide by being allowed to stand for some time in $\frac{N}{10}$ Na_2S solution.

As a mean of ten determinations the E.M.F. of the combination—

$$+ \text{Hg} \mid \text{Hg}_2\text{Cl}_2, \text{N. KCl} \parallel \text{N. KCl} \mid \text{0·1 mol. N } \text{Na}_2\text{S} \mid \text{Ag}, -$$

was found to be 0·880 ± 0·004 volt. The potential of $Hg \mid Hg_2Cl_2$, N. KCl is +0·283 volt (hydrogen standard), therefore that of Ag | 0·1 mol. N. Na_2S is − 0·597 volt. The formula—

$$E = P + \frac{RT}{nF} \log_e C,$$

where E is the potential of a metal in a solution in which the concentration of its ions is C, *n* the valency, and P the "normal potential" of the metal, enables us to calculate C. For 25° the formula becomes—

$$E = P + \frac{0·0590}{n} \log C.$$

For silver P is + 0·771 volt* (hydrogen standard), so that we have—

$$-0·597 = 0·771 + 0·0590 \log C.$$

* Wilsmore, *Zeitschr. f. physik. Chemie*, 35, 291.

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Hence C, the concentration of $Ag^{\cdot}$-ions in 0·1 mol. N. Na_2S solution saturated with $Ag_2S = 6{\cdot}3 \times 10^{-24}$ gm.-ion per litre.

In 0·1 mol. N. Na_2S solution the S''-ion concentration is 1×10^{-3} gm.-ion per litre, therefore the solubility-product of Ag_2S—

$$[Ag^{\cdot}]^2[S''] = (6{\cdot}3 \times 10^{-24})^2 \times 10^{-3} = \underline{3{\cdot}9 \times 10^{-50}}.$$

Since in a saturated aqueous solution of Ag_2S, $[S''] = \frac{[Ag^{\cdot}]}{2}$, we may write the solubility-product in the form—

$$\tfrac{1}{2}[Ag^{\cdot}]^3 = 3{\cdot}9 \times 10^{-50},$$

whence—

$$[Ag^{\cdot}] = 4{\cdot}3 \times 10^{-17} \text{ gm.-ion per litre.}$$

This is the concentration of the $Ag^{\cdot}$-ions in a saturated aqueous solution of Ag_2S at 25°, and, if we assume that dissociation is complete, the solubility of Ag_2S in water at 25° is $2{\cdot}2 \times 10^{-17}$ gm.-mol. per litre.

PbS.—The electrode was a rod of pure lead.

As a mean of seven determinations the E.M.F. of the combination—

$$+ \text{ Hg } | \text{ } Hg_2Cl_2, \text{ N. KCl } | \text{ N. KCl } | \text{ 0·1 mol. N. } Na_2S \text{ } | \text{ Pb } -$$

was found to be 0·773 ± 0·003 volt. Therefore—

$$\text{Pb } | \text{ 0·1 mol. N. } Na_2S = -0{\cdot}490 \text{ volt,}$$

and—

$$-0{\cdot}490 = -0{\cdot}148 + 0{\cdot}0295 \log C,^*$$

whence C, the concentration of $Pb^{\cdot\cdot}$-ions in 0·1 mol. N. Na_2S saturated with $PbS = 2{\cdot}6 \times 10^{-12}$ gm.-ion per litre. The solubility product of PbS is, therefore, $[Pb^{\cdot\cdot}][S''] = \underline{2{\cdot}6 \times 10^{-15}}$, the concentration of $Pb^{\cdot\cdot}$- or S''-ions in a saturated aqueous solution of PbS at 25° = $5{\cdot}1 \times 10^{-8}$ gm.-ion per litre, and the solubility of PbS in water at 25°, assuming complete dissociation, = $5{\cdot}1 \times 10^{-8}$ gm.-mol. per litre.

CuS.—The electrode was a platinum point electrolytically coated with copper, and was used either when freshly prepared or after being converted into CuS by immersion for some time in a 0·1 N. solution of Na_2S.

As a mean of twelve determinations the E.M.F. of the combination—

$$+ \text{ Hg } | \text{ } Hg_2Cl_2, \text{ N. KCl } | \text{ N. KCl } | \text{ 0·1 mol. N. } Na_2S \text{ } | \text{ Cu } -$$

was found to be 1·102 ± 0·003 volt. Therefore—

$$\text{Cu } | \text{ 0·1 mol. N. } Na_2S = -0{\cdot}819 \text{ volt,}$$

and—

$$-0{\cdot}819 = 0{\cdot}329 + 0{\cdot}0295 \log C,^\dagger$$

whence C, the concentration of $Cu^{\cdot\cdot}$-ions in 0·1 mol. N. Na_2S solution saturated with CuS, = $1{\cdot}2 \times 10^{-39}$ gm.-ion per litre. The solubility-product of CuS is, therefore, $[Cu^{\cdot\cdot}][S''] = \underline{1{\cdot}2 \times 10^{-42}}$, the concentration of $Cu^{\cdot\cdot}$- or S''-ions in a saturated aqueous solution of CuS at 25° = $1{\cdot}1 \times 10^{-21}$ gm.-ion per litre, and the solubility of CuS in water at 25°, assuming complete dissociation = $1{\cdot}1 \times 10^{-21}$ gm.-mol. per litre.

For completeness the figures for HgS, as determined by the investigation of its complex formation with Na_2S, may be given here. The solubility-pro-

* Wilsmore, *Zeitschr. f. physik. Chemie*, 35, 291.
† Wilsmore, *Ibid.*

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duct $[Hg^{\cdot\cdot}][S'']$ = $2{\cdot}8 \times 10^{-54}$, the concentration of the $Hg^{\cdot\cdot}$- or S''-ions in a saturated aqueous solution of HgS at 25° = $1{\cdot}7 \times 10^{-27}$ gm.-ion per litre, and the solubility of HgS in water at 25°, assuming complete dissociation, = $1{\cdot}7 \times 10^{-27}$ gm.-mol. per litre.

SUMMARY.

The results of this investigation may be summarised as follows :—

(1) The solubility of HgS in solutions of Na_2S, K_2S, and BaS has been determined.

(2) Of the two forms of HgS, black and red, the black modification has been shown, by its greater solubility in Na_2S solutions, to be the unstable form.

(3) The influence of temperature on the solubility of HgS in Na_2S was found to be small. The temperature-coefficient between 25° and 33° is negative. The effect of adding NaOH to the Na_2S solutions is greatly to increase the solubility of HgS, owing to the diminished hydrolysis of Na_2S.

(4) The solubility of HgS in Na_2S solutions has been found to depend on the formation of the complex anion HgS_2''. The constant for the formation of the complex from the ions $Hg^{\cdot\cdot}$ and S'' is—

$$k_2 = \frac{[HgS_2'']}{[Hg^{\cdot\cdot}][S'']^2} = 5{\cdot}1 \times 10^{54}.$$

(5) The solubility of HgS in Na_2S_2 solutions was found to be about half that in the corresponding Na_2S solutions. The same complex anion HgS_2'' probably predominates in both solutions.

(6) The hydrolysis of Na_2S in dilute solution has been shown to be practically complete.

(7) From the hydrolysis-constant of Na_2S the second dissociation-constant of H_2S has been calculated. With the aid of the various constants obtained in this investigation the concentrations of the S''- and other ions in various sulphide solutions have been calculated.

(8) A double sulphide of sodium and mercury, having the formula $2Na_2S.5HgS.3H_2O$, has been prepared and analysed.

(9) The solubility-products of HgS, Ag_2S, CuS, and PbS have been determined.

A large part of this investigation was carried out in the laboratory of Professor Dr. R. Abegg, Breslau, and it is with great pleasure that I take this opportunity of thanking Professor Abegg for his valuable advice and assistance.

CHEMICAL DEPARTMENT,
ABERDEEN UNIVERSITY.

DISCUSSION.

Professor R. Abegg (*communicated*) said he had nothing to add to the Paper, but he would like to offer the author his sincere congratulations on his extremely interesting and valuable results, which gave at last a quantitative basis to what had long been a merely qualitative treatment of an important analytical reaction.

Dr. F. Mollwo Perkin referred to the bearing of the Paper on analytical problems. It was well known in analytical chemistry that a large excess of sodium or ammonium sulphide should not be employed

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when dissolving out the sulphides of the arsenic group, owing to the tendency for the sulphides of copper and mercury to go into solution. Dr. Knox, in his Paper, shows from physical considerations what that solubility is. With reference to the relative solubility of red and black mercuric sulphide, the author shows the red to be the stable modification. This is, of course, only what was to be expected, seeing that on leaving the black modification in contact with a little sodium sulphide and free alkali in a short time complete transformation into the red modification takes place.

Dr. V. H. Veley endorsed what the Chairman had said regarding the points of considerable interest presented by the Paper in connection with the precipitation of the heavy metals by hydrogen sulphide.

With regard to the best conditions of acidity for the precipitation of sulphides mentioned in the paper (p. 46, par. 7), it was very usual in practice to make the solution far too acid.

Physico-chemical Papers, like that of the author, certainly helped one to understand and carry out even the ordinary routine work of the laboratory; only those who knew the difficulties of manipulation in sulphide precipitations, for example, could really appreciate this fact.

Dr. G. Senter asked whether Dr. Knox, in the course of his solubility determinations with sulphides, had experienced any difficulty in attaining the same equilibrium point from both sides. It was well known, and had been shown again quite recently by Glixelli (*Abstracts Chem. Society*, 1907, ii. 868) for zinc sulphide, that "false equilibria" are very frequent in sulphide solutions.

Dr. A. C. Cumming pointed out that on page 44 of the paper a case such as was spoken of by Dr. Senter was referred to.

Dr. J. Knox (*communicated reply*): The figures given for the concentrations of the different ions in various sulphide solutions, referred to by Dr. Veley, are not intended to represent the best conditions for sulphide precipitation, but merely to indicate approximately the relations between the concentrations of the ions in average cases. The best conditions for precipitation will, of course, be different for different sulphides. In reply to Dr. Senter, I may say that no indication of "false equilibrium" was obtained, and that in the several cases tried the same equilibrium point was reached from both sides.

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THE PLANIMETRIC ANALYSIS OF ALLOYS, AND THE STRUCTURE OF PHOSPHOR-COPPER.

By A. K. HUNTINGTON and C. H. DESCH, D.Sc., Ph.D.

(*A Paper read before the Faraday Society, Tuesday, April* 28, 1908, Dr. T. M. Lowry *in the Chair.*)

In the microscopic examination of metallic alloys, a smooth surface prepared by grinding and polishing is treated chemically in such a way as to differentiate between the structural constituents, and so to render the arrangement visible to the eye. This differentiation may be brought about by means of an attack by a solvent, which, dissolving one constituent more than another, produces differences of level which become visible on illumination, or by means of a reagent forming surface films of oxide or sulphide, so that differences of colour are produced. In both cases the contrasts of light or colour make visual and photographic examination of the specimen possible. Valuable qualitative information is thus obtained as to the number, character, and arrangement of the structural constituents of the alloy, and in many cases the previous mechanical and thermal treatment of the specimen may be inferred. But in certain cases the examination may be carried a stage further, and may be utilised to yield quantitative information, so as to indicate the proportions in which the component metals are present, the nature of those metals being supposed to be known.

On examination of the polished and etched section one or other of the following conditions may present itself:

1. The section exposed is homogeneous, containing only one structural constituent. This may show division into crystal grains, without, however, any intercrystalline cementing material. Owing to differences in the orientation of neighbouring grains, contrasts may appear under oblique illumination, but after a little experience there is no danger of confusion with the case of more than one micrographic constituent. The specimen may be:

   a. A pure metal;

   b. A definite intermetallic compound; or

   c. A homogeneous solid solution.

   In case *a*, the information obtained is definite. Thus in the alloys of lead and tin, or of gold and thallium,* which do not form either compounds or solid solutions with one another, the only members of the series which present a homogeneous appearance under the microscope are the pure metals. The addition of even a small quantity of the second metal brings about the appearance of a second micrographic constituent, the absence of which is a proof of the purity of the metal.

   In case *b*, the composition is also definite. For instance, magnesium

* Levin, *Zeitsch. Anorg. Chem.* 1905, **46**, 49.

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forms with tin the compound Mg_2Sn,* which does not form solid solutions with either magnesium or tin. An alloy, therefore, containing 29 per cent. Mg and 71 per cent. Sn, corresponding with the formula Mg_2Sn, is homogeneous, and an increase in the proportion of either tin or magnesium brings about the appearance of a second constituent.

In case *c*, the composition is indeterminate. When the two metals are isomorphous, the entire series of their alloys is homogeneous, and microscopic examination gives no clue to the composition. Such pairs of metals are gold and silver, iron and manganese, and cobalt and nickel. When, however, the solubility of one component in the other in the solid state is limited, so that there is a gap in the series of mixed crystals, a homogeneous structure indicates that the composition of the alloy falls within certain limits, which may in some cases be very narrow. Thus silver dissolves aluminium at the ordinary temperature up to a limit of 4 per cent. Al, any further increase of aluminium becoming apparent by a separation into two constituents.† In the case of the cadmium-gold alloys, between the compounds Au_4Cd_3 and $AuCd_3$, a series of solid solutions is formed containing from 51 to 63 per cent. Cd.‡

2. Two solid constituents are visible in the same section. If the composition of the two phases is known, a measurement of the relative areas occupied by them, in the manner described below, gives by calculation the proportions in which the two components are present. A good example of this case is presented by the copper-zinc alloys containing from 36·5 to 46·5 per cent. Zn, sections of which exhibit two micrographic constituents, the so-called α and β solutions.
3. The alloy is a eutectic mixture. Two solid phases are then present, mechanically intermixed in an intimate fashion, and since the eutectic formed by any given pair of phases has always the same composition, the composition of the alloy is known.
4. Crystals of a solid constituent are surrounded by a eutectic. The composition of the eutectic being constant, it may, although heterogeneous in structure, be treated as a single constituent, with certain exceptions to be discussed later. Measurements of the relative areas occupied by crystals and eutectic may then be made as in case 2.

It is essential to the application of this method that the alloys shall be in a known condition of equilibrium, that is, they must either have been cooled so slowly that sufficient time has been allowed for equilibrium to have been established between the solid phases, or if quenched, the conditions of equilibrium at the temperature of quenching must be known. The method of quantitative microscopic measurement is therefore only applicable to alloys of which the freezing-point and transformation curves have been accurately determined. In general, this is only true of alloys which have been investigated by Tammann's method of thermal analysis,§ the mere determination of the liquidus curve being insufficient. This method consists in observing the time occupied by each arrest in the cooling curve of an alloy. Thus, in an alloy containing a eutectic, there will be an arrest in the cooling curve at the temperature of solidification of the eutectic, and the duration of that arrest will depend on the proportion of eutectic present.

* Grube, *Zeitsch. anorg. Chem.*, 1905, **46**, 76; Kurnakoff and Stephanoff, *ibid.*, 177.

† Petrenko, *Zeitsch. anorg. Chem.*, 1905, **46**, 49.

‡ Vogel, *Zeitsch. anorg. Chem.*, 1906, **48**, 333.

§ Tammann, *Zeitsch. anorg. Chem.*, 1903, **37**, 303; 1905, **45**, 24.

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On plotting the duration of the arrest for a series of alloys of varying composition against the composition, the maximum time, obtained either directly or by interpolation, corresponds with the eutectic composition. In the same way, when a heat evolution is due to the enantiotropic change of a compound, the composition of the compound may be arrived at by plotting the duration of that heat evolution against the composition of a series of neighbouring alloys. It is in this way that the presence of definite compounds in a series of solid solutions may be detected. It must be remembered that equilibrium in solid alloys is often only gradually attained, the processes of diffusion and segregation being very slow, so that long annealing at a definite temperature may be necessary in certain cases.

In the actual carrying out of the method in cases 2 and 4 mentioned above, it is found that the ordinary photo-micrographs are on too small a scale to allow of accurate measurement. It is therefore necessary to enlarge them, or, more simply, to project the magnified image of the section by means of a horizontal photo-micrographic apparatus on to a sheet of paper pinned to a drawing-board placed vertically, and to trace the outlines of the constituents with a pencil. When, owing to the low reflecting power of the surface of the alloy, the illumination is insufficient for this purpose, or when a vertical camera is employed, it is better to replace the ground-glass screen of the camera by tracing paper laid on clear glass, and

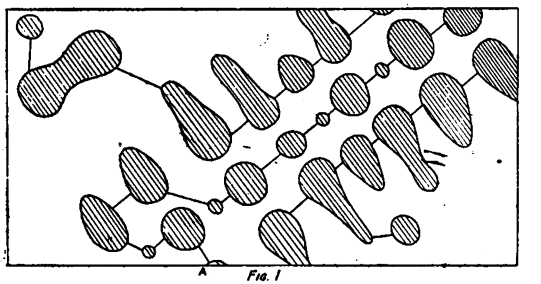

FIG. 1

to trace the outlines in that way. It is of course essential that the field chosen for projection shall be typical of the structure of the whole specimen, or, where the structure varies from one part of the specimen to another, several fields must be measured and the results averaged.

A tracing having been obtained by one or other of these methods, a boundary line is ruled so as to enclose the pattern to be measured. It will be found to facilitate measurement if the crystals of that constituent which has the most clearly developed outlines be shaded with pencil. The area of the shaded portions is then measured by means of a planimeter. A starting-point is marked on the margin as at A (Fig. 1) and the outline is then followed clockwise with the tracing point of the planimeter, passing from one detached outline to another along a straight line as shown in the figure, care being taken that the return journey is made over the same line. It is advisable to check the result, after taking the final reading of the planimeter, by retracing the outline in the opposite direction (counter-clockwise), when the dial of the planimeter should of course return to the initial reading.

When the pattern is very complicated, or made up of many small and detached portions, or when the outlines of the crystals are unusually intricate, the errors of the planimetric method may become greater than is permissible. In such cases, better results are obtained by ruling lines 1 cm.

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apart on the tracing, so as to divide the whole field into 1 cm. squares. After a little practice, it is not difficult to estimate the relative proportions of the shaded and white areas in any square, and the results are set down in order. Thus 0·7 indicates that the square is estimated to be shaded over seven-tenths of its area and white over three-tenths. The readings are added up separately and divided by the number of squares in the column, and the mean of all the results so obtained is taken. In this way a very close approximation to the true proportions may be obtained.*

Two other methods of obtaining the superficial areas of the constituents were met with when we had nearly completed this work, and may be mentioned here for the sake of completeness, although they are much less convenient than those described above. The first consists in cutting out the shaded portions of the tracing, either on paper alone or on paper with a tinfoil backing, and weighing the separated portions. This method was introduced by Delesse in 1847 for the purpose of determining the volume composition of igneous rocks, but is obviously not susceptible of as great accuracy as measuring with the planimeter. The second method, also employed by petrologists in the study of igneous rocks,† consists in drawing straight lines through typical fields, and measuring the intercepts of the different constituents upon these lines. Although this method gives sufficiently accurate results in the case of rock-sections, in which the minerals present usually form fairly compact and regular areas, it is less applicable to the more complex patterns which characterise the micro-sections of metallic alloys. It is easy to show that either of these methods, depending on the measurement of superficial areas or of linear intercepts, gives the true volume ratios of the constituents.

The examination of an alloy by this method occupies very little time. With practice it is possible to grind, polish, and etch a Muntz metal, for instance, in five minutes, using a Stead polishing machine driven by an electric motor, and the projection and planimetric measurement may be completed in half an hour. The method therefore possesses the advantage of great rapidity.

The proportions of the component metals corresponding with the areas exposed may be calculated from a knowledge of the densities of the constituents. It is possible, however, to dispense with this calculation by employing a graphical method already in use for metallographic purposes, and shown in Fig. 2. The diagram is constructed by taking as abscissæ the percentages of the component metals and as ordinates the percentage of the area occupied by any micrographic constituent. The diagonal lines are obtained by joining up points corresponding with the composition of each

* Comparison of Planimetric Measurements with Measurements by the Method of Squares.

No. of Specimen.	Condition.	Area of Crystals.		Phosphorus per cent.		
		Planimeter.	Squares.	Planimeter.	Squares.	Analysis.
403	As cast	31·4	28·6	10·08	9·9	9·89

Areas of crystals from about 25 per cent. to about 75 per cent. can be fairly accurately judged by the eye, *e.g.*, No. 403 given above was originally estimated at about 30 per cent.—the exact mean between the readings from the planimeter and from the method of squares.

† See J. W. Evans, *Quart. J. Geol. Soc.*, 1906, **62**, 116.

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micrographic constituent in order, the points being taken alternately on the top and bottom line. An ordinate erected at the composition of any given alloy will therefore, by its intersection with the diagonal, give at once the percentage area occupied by each constituent. Fig. 2 is constructed for the

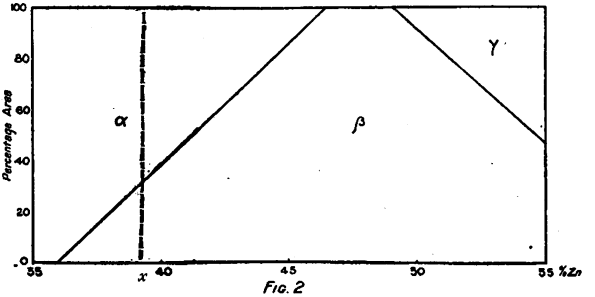

Fig. 2

copper-zinc alloys from the data of Shepherd.* The ordinate at the point x indicates that an alloy containing 61 per cent. Cu and 39 per cent. Zn will consist of 75 per cent. α and 25 per cent. β.

The use of the planimeter in the microscopic examination of metals has already been applied to the estimation of carbon in steels† by measurement of the areas occupied by the eutectoid perlite, which contains 0·9 per cent. C, and to that of oxygen in cast copper by measurement of the cuprous oxide eutectic areas.‡

The application of the method may be illustrated by the following examples :—

Alloy.	Constituents Present.	Area of one Constituent.	Calculated from Area.	Found by Analysis.
Cu — Al	$\alpha + \beta$	72·5% α	9·4	9·26% Al
Cu — Al	$\alpha + \beta$	49·0% α	10·2	10·97% Al
Cu — Al	$\beta + \delta$	48·6% δ	13·7	13·7% Al §
Cu — Zn — Sn ‖	$\alpha + \beta$		42·8	42·95
,,	$\alpha + \beta$		41·0	40·60
,,	$\beta + \gamma$		49·4	49·50
,,	$\alpha + \beta$		43·1	43·07
,,	$\alpha + \beta$		42·2	42·10

We have tested the method most fully in the case of the copper-phosphorus alloys. Phosphor-copper, containing about 10 per cent. P, was taken as the starting-point, and alloys richer in copper were prepared by fusion with electrolytic copper, the cast alloys being annealed in a Heraeus electric furnace. The alloys take a high polish, and when etched with dilute nitric acid develop a well-marked structure. The nature of the micrographic constituents in alloys containing from 0 to 15 per cent. P is shown in Fig. 3, the structures actually observed being shown by the photo-micrographs, Figs. 4–10, these being selected as typical of a large number actually taken.

* Shepherd, *J. Physical Chem.*, 1904, **8**, 421.
† Sauveur, *Metallographist*, 1898, **1**, 27.
‡ Heyn, *Zeitsch. anorg. Chem.*, 1904, **39**, 1.
§ Calculated with the aid of Guillet's diagram. *Rev. de Metall.*, 1905, **2**, 565.
‖ The calculations in the case of copper-zinc alloys containing tin has been made by means of Guillet's formula (*Rev. de Métall.*, 1906, **3**, 243).

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Copper retains up to 0·175 per cent. P in solid solution, but an increase in the quantity of phosphorus causes the appearance of a eutectic containing the phosphide Cu_3P. With increasing phosphorus, the eutectic increases in quantity at the expense of the copper crystals, which appear dark in the photographs. At 8·27 per cent. P the whole alloy consists of eutectic, and on still further increasing the phosphorus, rounded white crystals of the phosphide make their appearance, until at 14·09 per cent. P, corresponding with the compound Cu_3P, they fill the whole area. From 14·09 to 15 per cent. P, the limit obtainable under ordinary pressure, the alloys consist of a homogeneous solid solution.

The results of the planimetric measurement are shown in Fig. 3, the observed points being indicated by crosses. As will be seen, they are far from coinciding with the theoretical values, which should fall on the diagonal straight lines. When this work was nearly completed, a paper on the copper-phosphorus alloys by Heyn and Bauer appeared,* in which the series was

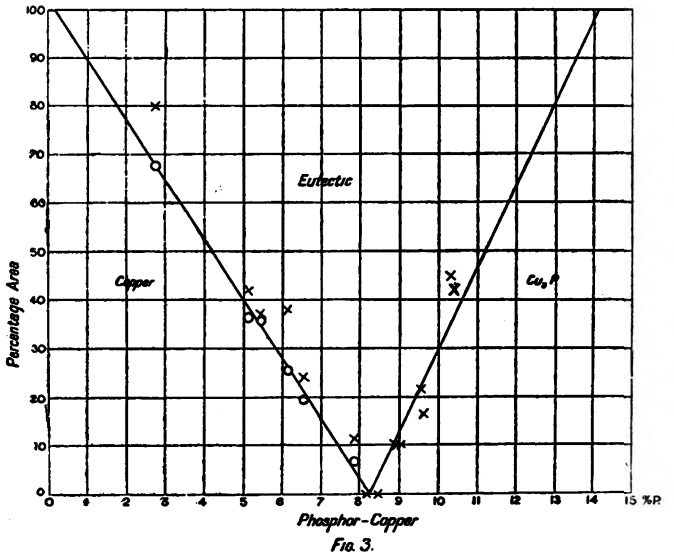

Fig. 3.

very thoroughly studied, and some planimetric measurements on the left-hand side of the eutectic in the diagram were made. These authors noted the same kind of deviation from the theoretical line, and constructed a curve to replace the diagonal for the purposes of practical measurement. They did not, however, attempt any explanation of the discrepancies. An examination of the photographs, Figs. 4–6, suggests the true explanation. As will be seen, the copper crystallites, which appear dark in the etched specimens, are surrounded by a belt of white copper phosphide, separating them from the copper-copper phosphide eutectic, easily recognised by its banded structure. The formation of this belt is due to segregation. It is well known that whe large and small crystals of a salt are in contact with its saturated solution the large crystals tend to grow at the expense of the smaller. The same thi has been observed in the case of solid solutions. When steel containing the eutectoid pearlite is maintained for a sufficient time at a suitable temperature,

* Heyn and Bauer, *Mitt. k. Materialprufungsamt*, 1906, **24**, 93 ; *Zeitsch. anorg. Chem.*, 1907, **52**, 129.

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FIG. 4.
2·73 per cent. P. × 300.

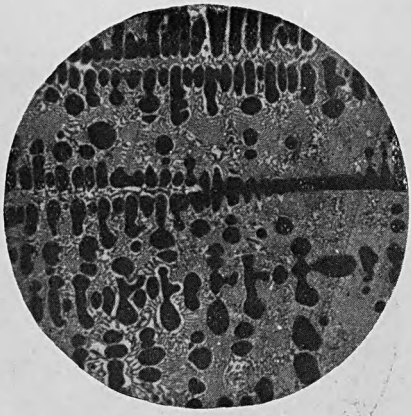

FIG. 5.
6·11 per cent. P. × 100.

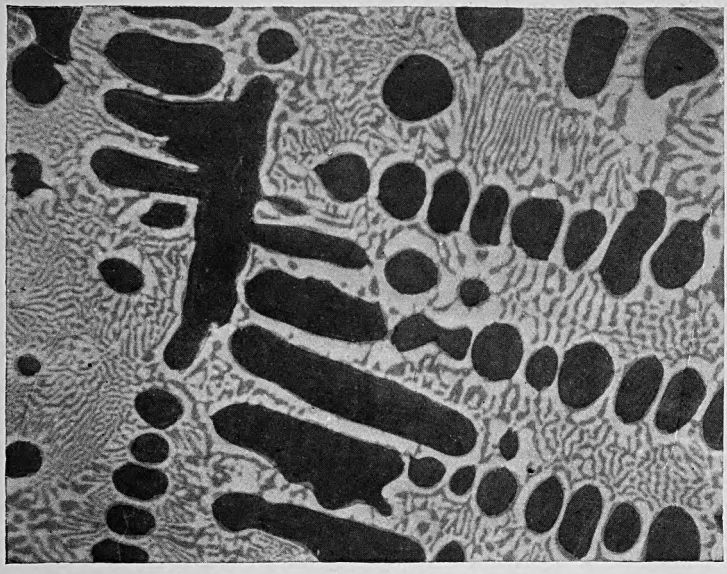

FIG. 6.
6·11 per cent. P. × 300.

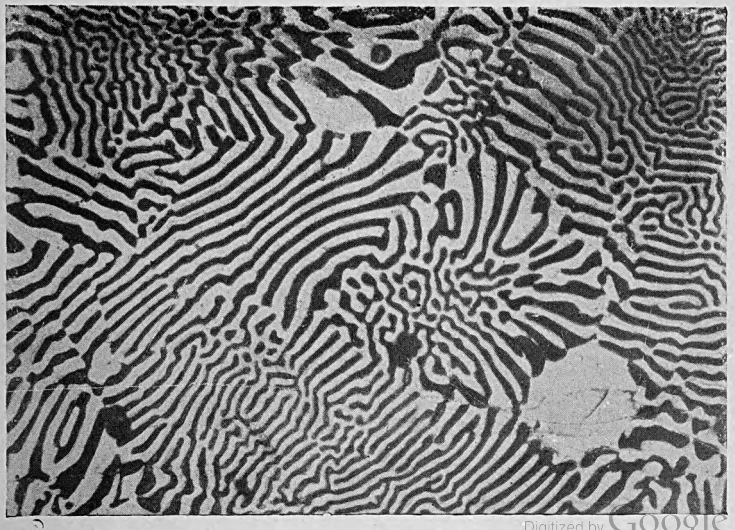

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FIG. 7.

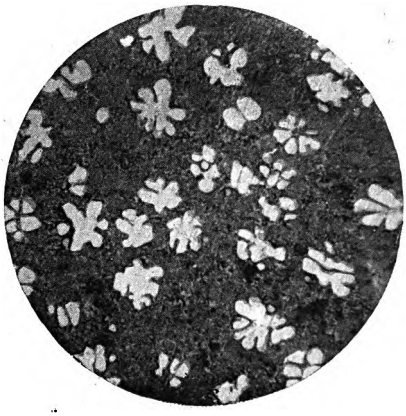

FIG. 8.
8·93 per cent. P × 100.

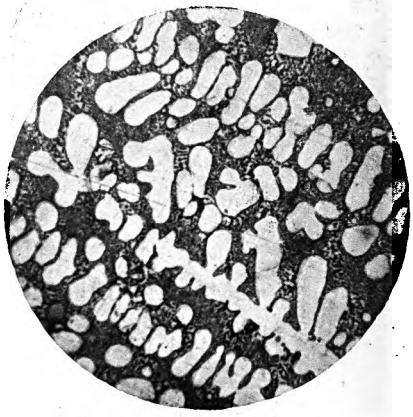

FIG. 9.
10·30 per cent. P. × 100.

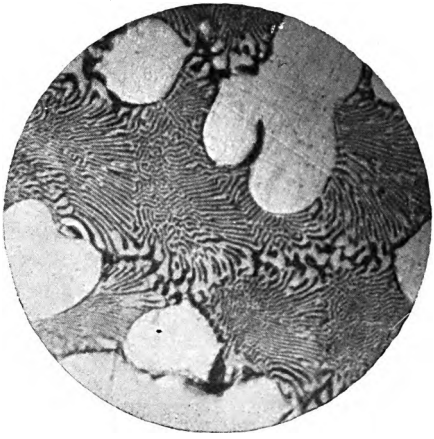

FIG. 10.
10·30 per cent P × 300.

FIG. 11.
Ag. Cu. × 300.

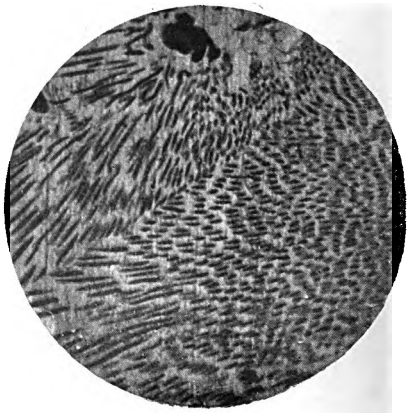

FIG. 12.
Ag. Cu eutectic. × 300.

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the pearlite becomes coarser, and in time the segregation becomes complete, the component structural elements of the pearlite, namely, ferrite and cementite, being entirely separated, so that masses of pure cementite occupy the positions originally occupied by perlite. The formation of a clear belt around crystals may be observed in certain igneous rocks, such as perlites. The crystals at first formed in the process of devitrification of the glassy magma attract to themselves the minute dust-like crystallites in their immediate neighbourhood, leaving a clear space, called by petrologists the "Krystallisationshof," which is thus correspondingly poorer in the mineral which has first crystallised than the mass of the rock. In the case of phosphor-copper the result of the segregation is that the copper crystals occupy an area greater than that corresponding with the equilibrium. They have drawn to themselves a part of the copper of the surrounding eutectic.

It is possible to correct for this segregation in the following manner. The white belt of copper phosphide is a measure of the amount of segregation which has taken place, and it is therefore necessary to make planimetric measurements, not only of the copper areas, but also of the enveloping belt of phosphide.

The two components of the eutectic are copper phosphide, Cu_3P, containing 14·09 per cent. P, and a solid solution of phosphorus in copper, containing 0·175 per cent. P. As the eutectic contains 8·27 per cent. P, its composition by weight is given by the equation:

$$14{\cdot}09x + 0{\cdot}175(100 - x) = 100 \times 8{\cdot}27,$$

or $x = 57$; that is, the eutectic is made up of 57 parts by weight of Cu_3P and 43 parts of the solid solution of phosphorus in copper. The specific gravities of the solid solution and of copper phosphide being given by Heyn and Bauer (*loc. cit.*) as 8·86 and 7·18 respectively, the eutectic must contain 62 per cent.

Number.	Fig.	Structure.	Area of Crystals. Per Cent.	Corrected Area. Per Cent.	Per Cent. P by Planimetric Measurements.	Per Cent. P by Analysis.
225	4	Cu + eutectic	80·0	67·8	2·75	2·73
227		" "	42·0	36·4	5·30	5·08
226	5 and 6	" "	37·8	25·7	6·15	6·11
216		" "	37·0	36·0	5·38	5·45
205		" "	24·0	19·3	6·65	6·55
202		" "	11·2	6·8	7·60	7·88
224	7	All eutectic	—	—	8·27	8·25
204		" "	—	—	8·27	8·50
201	8	Cu_3P + eutectic	10·0	—	8·85	8·93
203		" "	10·0	—	8·85	9·05
222		" "	16·6	—	9·28	9·64
241		" "	21·8	—	9·50	9·59
199	9 and 10	" "	45·0	—	10·9	10·30
271		" "	43·0	—	10·8	10·70

of Cu_3P and 38 per cent. of the solid solution by volume. This will also be the ratio of the superficial areas occupied by the two phases in a microscopic section. A belt of segregated phosphide, therefore, corresponds with $\frac{38}{62} = 0{\cdot}61$ of its own area of copper, and this amount has accordingly to be deducted from the measured area of the copper crystals (properly crystals of the solid solution, containing a small amount of phosphorus) in order to arrive at the true area. The results obtained are shown in the table above, in which

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the areas given are usually the mean of several concordant measurements. The corrected points are shown in Fig. 3 as circles. It will be noticed that the correction for segregation, in the case of alloys containing free copper, is large, but that when this is taken into account the percentages of phosphorus estimated planimetrically are in remarkably close agreement with those found by analysis. When the phosphorus content is low, as in the first alloy in the table, no eutectic structure is visible, the copper crystals being separated by clear areas of phosphide, from which all the intermixed copper has been withdrawn by segregation (Fig. 4).

In the case of the alloys containing free copper phosphide, segregation of the kind described above does not take place, and the crystals of Cu_3P are in immediate contact with the beautifully laminated eutectic. The area of the phosphide crystals found by the planimeter tends to be higher than that corresponding with the analysis when the percentage of phosphorus is high. This appears to be due to imperfect equilibrium in the process of solidification, the separation of crystals along the copper phosphide branch of the freezing-point curve being continued beyond the eutectic point, owing to the failure of the second constituent to crystallise. Such super-fusion is frequently observed, and its effect on structure has been recently discussed for the cases of organic mixtures and igneous rocks, by Prof. Miers & Miss Isaac.*

The copper-phosphorus alloys are not the only examples of segregation giving rise to a band surrounding the crystals first formed. The phenomenon is well observed in the alloys of silver and copper, the constituents of which are two solid solutions, the one rich in copper, the other in silver (Figs. 11 and 12). The outer boundary of the segregated silver-rich band is, however, too indefinite to allow of satisfactory planimetric measurement.

In dealing with metals which have been slowly cooled from the fused state, so as to allow sufficient time for the attainment of equilibrium, the planimetric method may be found of considerable practical use, especially in routine work, in which the alloys dealt with are only liable to vary within comparatively narrow limits. When the proper conditions are fulfilled, the accuracy is sufficient for all practical purposes. The method may also find application in the investigation of new series of alloys, when it is necessary in any case to anneal the specimens so thoroughly as to ensure equilibrium, and the planimetric measurements of the proportions in which the micrographic constituents occur may be found to be a valuable check on the results of thermal analysis.

In conclusion, we wish to express our thanks to Mr. A. B. Licence for assistance in the planimetric measurements, and to Miss E. A. Macadam, A.I.C., who made the chemical analyses quoted in the paper.

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DISCUSSION.

Professor W. W. Haldane Gee (*communicated*). The method adopted by Professor Huntington and Dr. Desch seems likely to be of considerable practical importance. It might be used to compare the relative losses of the constituents of an alloy after prolonged etching with different reagents, and so help to throw light on the method of corrosion. It would be

* Miers & Isaac *Proc. Roy. Soc.* 1907 **79**A, 322.

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of especial interest to apply planimetric analysis to alloys which had been electrolytically corroded by being made anodes in various salt solutions.

Professor A. K. Huntington said further extension of the method would probably be made to the case of the phosphor-tin alloys as soon as the curves had been arrived at. He thought the method—apart merely from its analytical value—gave an insight into the structural composition of a metal not revealed by chemical analysis.

Dr. C. H. Desch said it was not claimed that the method was of universal applicability; for example, in many low percentage bronzes the metal was homogeneous, and an inspection of the structure therefore gave no information as to the composition. Again, it was necessary for the alloy to be in a state of physical equilibrium—slow, solid diffusion often took place even after annealing had been continued for some time, and he had been much struck by this in commercial alloys. The chief point of scientific interest in the paper that he would like to accentuate was the effect of segregation. This had not been studied quantitatively before, and was, he believed, more general in alloys than was usually supposed.

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THE INTERACTION OF ALUMINIUM POWDER AND CARBON.

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

(*A Paper read before the Faraday Society, Tuesday, April* 28, 1908, Professor A. K. Huntington, Vice-President, *in the Chair.*)

In attempting to remove the grease with which aluminium powder is coated by gently heating, it was noticed that a black deposit was formed on the surface of the powder, accompanied by an evolution of heat with incandescence; as the temperature of heating was not above 400° C., it was thought probable that the aluminium powder had attacked the vapour produced from the grease, with the production of a carbide of aluminium* differing from that formed by Moissan in the electric furnace at a very high temperature. Very little information on the direct union of aluminium and carbon, without the use of the electric furnace, is available, and even that which has been published is vague, and in some cases contradictory. Moissan† states: "According to Mallet aluminium does not combine with carbon; on the other hand, Franck, by calcining a mixture of aluminium and lampblack, obtained a metallic substance yielding hydrogen contaminated with acetylene when treated with hydrochloric acid." ‡ Mallet's statement need not be considered in view of the fact that fine aluminium powder was not used or procurable, and for a similar reason the amount of carbide produced by Franck was small.

Franck§ prepared a small quantity of aluminium carbide by heating aluminium powder in carbon monoxide or carbon dioxide, and confirmed the experiments of Guntz and Moissan.|| He also made aluminium react with lampblack, producing a body which evolved a large amount of methane with water.

Fritz Fichter,¶ using a mixture of aluminium powder and soot, prepared an impure aluminium nitride as follows: A mixture of aluminium powder with 4 to 5 per cent. of soot was made and heated to a high temperature; it was then exposed to the air, when a vigorous action took place, producing a fairly large yield of aluminium nitride.

Kusnetzkoff** showed that aluminium at temperatures near its melting-point decomposes CH_4, C_2H_6, C_2H_4, and C_2H_2 completely into their elements. The H and part of the C are obtained in the free state, whilst the remainder of the carbon forms aluminium carbide.

Matignon†† states Berthelot has shown that a large disengagement of heat takes place when aluminium and carbon react; and, therefore, since the reaction is exothermic, combination ought to take place without the aid of an

* A gas with odour of acetylene was evolved in treating a portion with water.
† *The Electric Furnace* (1904), p. 235, in a footnote.
‡ See also *Bull. Soc. Chim.*, 1894 [3], 11, pp. 439–446.
§ *Ch. Zeitung*, 1898, p. 236. || *C. R.*, cxxiv., No. 4, 1897.
¶ *Zeitsch. Anorg. Chem.*, 1907, 54, pp. 322–327.
** *Ber.* 1907, 40, pp. 2871–2873. †† *C. R.*, cxlv., No. 17, 1907

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electric furnace. Matignon showed that the two elements would combine when heated in a Perrot furnace, forming an olive-green or yellow product. He used lampblack, and obtained an intimate mixture by working the two together with terebenthene, the proportion of lampblack to aluminium being 24 to 70 or 140 ; Al_4C_3 requires 24 of carbon to 72 of aluminium. When the large excess of Al was used the action could be started by igniting the mixture in one place, when it spread throughout the mass. The product gave on treating with water a gas consisting of 96·36 per cent. CH_4 and 3·36 per cent. H. As will be shown later by the authors, the product of reaction must have contained nitride.

In a letter to the *Chem. News*, November 29, 1907, the authors call attention to the fact that a mixture of aluminium powder and wood charcoal could be made to react with a fuse of Mg and BaO_2, similar to the ordinary thermite reaction. The authors now present in this paper the results of their investigations on the interaction of aluminium powder with wood charcoal, sugar charcoal, and graphite respectively. With each kind of carbon it was found possible to prepare a mixture with aluminium powder which, when started with a fuse of Mg powder and BaO_2, would react with vivid incandescence throughout the mass, similarly to the ordinary thermite reaction, the action being most pronounced in the case of wood charcoal. Mixtures which would not react with a fuse were found to do so when placed in a muffle furnace and heated to temperatures varying from 400° C. to 1,100° C. In some cases it was found that on heating the mixture in a closed Hessian crucible to dull redness, and then withdrawing the crucible and opening to the air, vigorous action took place throughout the mass, starting at the surface and proceeding downwards. In all cases the product of the reaction was found to contain the following: aluminium carbide, aluminium nitride, aluminium oxide, carbon, and aluminium. The percentage of Al_2O_3 produced varied from 10 to 55, not only in the different mixtures, but in different parts of the same mixture. All the products gave with water mixtures of CH_4 and H, the former produced by the action of water on the aluminium carbide Al_4C_3, viz.—

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4,$$

whilst the H was produced by the action of free Al in water in the presence of the NH_3 liberated by the action of water on the aluminium nitride.* Since CH_4 was the only hydrocarbon obtained either by the action of water or hydrochloric acid, the authors conclude that the only carbide formed in the reactions mentioned is the one described by Moissan, viz., Al_4C_3.†

The authors are of opinion that in all the reactions between aluminium and carbon mentioned above the air plays a most important part; the first action being the oxidation of the carbon to CO and CO_2,‡ thus producing sufficient heat to cause the oxidation of the Al powder to Al_2O_3, and this latter reaction raising the temperature sufficiently high to cause combination between the aluminium and the carbon, as well as the aluminium and nitrogen, the nitrogen coming from both the atmosphere and the occluded gases in the carbon. That the reason assigned is most probable follows from the following experimental facts:

* See later.

† This result confirms that of W. H. Patterson (*Chem. News*, December 20, 1907), who prepared aluminium carbide in the electric furnace at different temperatures, and could only obtain the carbide Al_4C_3.

‡ Pring (*J. C. S.*, October, 1905, p. 1532), in preparing aluminium carbide in the electric furnace, considers it is formed by action of Al on CO and CO_2 from the furnace gases.

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1. The reaction was most vigorous in the case of wood charcoal. All the mixtures of Al and wood charcoal were extremely porous, and hence contained plenty of air; also the volume of the carbon was greater proportionately to the aluminium in these mixtures than in the others; moreover, the wood charcoal contained ten times its own volume of occluded gases consisting of O and N.
2. Mixtures of aluminium and carbon which reacted with a fuse, when exhausted with a Töpler pump and heated to a full red heat, underwent very slight change.*
3. Mixtures of Al and C (all kinds) when heated in a current of air reacted before temperature had risen to a visible red heat, and the reaction continued throughout the mass. The products always contained carbide, nitride, and oxide, the latter two predominating under these conditions.

EXPERIMENTAL.

SERIES I.

Aluminium and Wood Charcoal.

The aluminium powder used was the finest obtainable from the British Aluminium Company. It was freed from its adherent coating of grease by extraction with ether and dried in a steam oven. The wood charcoal used was first heated for an hour in a closed tin at a temperature of about 1,000° C.; allowed to cool, powdered, and sieved. After passing through a 40,000-mesh sieve, it was again separated into a fine and coarse portion by means of a Goreham-Griffin flourometer to which a special receiver was fitted to collect the fine powder; this fine powder was used in the experiments. On igniting a weighed portion of the wood charcoal in a muffle, a brown residue was obtained which was 3 per cent. of the charcoal taken.

Three sets of mixtures were made up, having compositions represented by the following: (1) 4 Al to 3 C; (2) 4 Al to 6 C; (3) 8 Al to 3 C.

Mixture containing 4 *Al to* 3 *C.*

1. The mixture was placed in a Hessian crucible and a fuse of Mg powder and BaO_2 powder placed on top; into this a piece of Mg ribbon was put and lighted. The reaction commenced slowly at first, but then proceeded with increasing vigour and incandescence throughout the mass. It was found that the reaction took place best when the fuse was spread all over the surface, thus showing that a good heat supply must be available in order to start the action.
2. The mixture was placed in a porcelain basin and gently heated over a Bunsen burner. In five minutes a slight glow appeared at the bottom of the basin and slowly spread throughout the mass, and on reaching the upper surface bright incandescence took place, due to the burning of the Al in air. On cooling and examining the contents of the basin, a white layer $\frac{1}{16}$ in. thick completely covered the top, whilst below was found a greyish-black solid mass; no Al was visible.
3. The mixture, in a Hessian crucible, was placed in the front part of the muffle furnace and heated to about 400° C. After a few minutes a glow appeared on the top, when the crucible was withdrawn; the reaction spread throughout the mass slowly.

* See analyses, p. 69.

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4. The mixture was placed in a Hessian crucible, covered with a piece of asbestos cardboard, and then tightly packed with a layer, ¾ in. thick, of finely powdered MgO. Two crucibles were prepared and placed at the back of the muffle, which was at a temperature of between 1,000° and 1,100° C. One was left there two hours; the other was withdrawn at the end of five minutes and immediately opened; the contents instantly became incandescent.

Mixture containing 4 *Al to* 6 *C.*—This mixture could not be made to react with a fuse. The mixture was placed in a Hessian crucible and covered as before and heated half an hour at a temperature of about 1,000° C. On cooling the resulting mass was found to be soft and easily removable; at the top was found a very thin layer of Al_2O_3.

Mixture containing 8 *Al* + 3 *C.*—This mixture would not react in the cold with a fuse, but on heating in a crucible over a Bunsen the reaction took place easily. The mixture, placed in a Hessian crucible and covered as before, was heated for fifteen minutes at about 1,000° C. After five minutes CO appeared, and burnt, at a crack near the bottom of the crucible, and the crucible could be seen getting visibly hotter; CO also burnt on the top of the crucible. On cooling and opening the contents of the crucible were quite hard and crystalline, and at the top and near the crack a very thin layer of Al_2O_3 was found.

The products obtained in all the above experiments were more or less greyish-black in colour, and the core contained in all cases distinct yellowish crystals.

In no case were the contents of the crucibles the least disturbed, showing that very little gaseous products had been produced, but that combination between the carbon and aluminium had taken place.

On treating the powdered residue with water no action took place for some five to ten minutes; after this a gas was slowly evolved, but at a gradually increasing rate, and in the cases where only a small quantity of water was used a very violent evolution of gas took place after a short time and the flask became very hot. Using a large excess of water, no heating took place, and the gas was steadily and very slowly evolved for several weeks (in one case six weeks, another twelve, &c.). The solutions smelt strongly of NH_3, especially after a day or two, and the gas had a slight odour of acetylene and burnt readily with a slight whitish flame. The gas was fully analysed, and contained less than 0·2 per cent. of acetylene or other unsaturated hydrocarbons (see analyses). When the generating flask was placed in hot water the action was immediately vigorous. The solid products, therefore, contained carbide and nitride as well as aluminium, &c. After several attempts at analysing the solid the following process was adopted, which, although not of a high degree of accuracy, is sufficiently accurate to show the difference between the constitution of the products obtained in the various reactions.

Method of Analysis of the Crude Product of Reaction.

1. *Estimation of Free Aluminium.*—0·1 to 0·3 grm. of the substance, after crushing and sieving through 40,000-mesh sieve, was placed in ice-cold conc. HCl, kept well cooled in ice and salt, and thoroughly and continuously shaken for twenty minutes (see Moissan, *Electric Furnace*). The evolution of gas was fairly rapid at first, but at end of ten minutes was almost over. The solution was diluted with ice-cold water, filtered at the pump, washed with ice-cold water, and the dissolved Al in the filtrate estimated in the usual manner with NH_4OH. This treatment dissolved free Al, but left undissolved the whole of the carbide, nitride, and alumina. Comparative tests were made.

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2. *Estimation of Free C, Al_2O_3, Al_4C_3, and AlN.*—This involved two distinct processes, viz. :

A. About 2 grms. of substance—ground, &c., as in 1—were boiled in a conical flask for two to three hours with equal vols. of conc. HCl. and water (100 c.c.). The prolonged boiling is necessary in order to dissolve that carbide and nitride which are protected with a layer of Al_2O_3. H and CH_4 escape rapidly at first and then slowly for a time. At end of time stated the solution was diluted and filtered at the pump through a tared filter-paper and residue well washed:—washing collected with original filtrate. The residue, which is black, was dried and weighed to constant weight. This residue consists of C, Al_2O_3, and traces of SiO_2 (found to be very small and hence neglected); it was placed in muffle and burnt till quite white and to constant weight. This process burns off the C. It was observed early in the work that when the boiling with the HCl was not prolonged the residue gained weight on ignition, showing the presence of unacted upon carbide and nitride, viz. :

$$Al_4C_3\,(144) \longrightarrow 2\,Al_2O_3\,(204) \text{ and } 2\,AlN\,(82) \longrightarrow Al_2O_3\,(102).$$

The filtrate contained $AlCl_3$ (and traces of $FeCl_3$) derived from action of HCl in the free Al, the Al_4C_3, the AlN, as well as some of the Al_2O_3 (see note). It was evaporated to dryness in a water-bath, redissolved in water, and again evaporated to dryness with NH_4OH, and then ignited in the muffle in a tared basin; the Al_2O_3 thus obtained was weighed. The residue obtained was always found to be quite white, though it contained traces of Fe_2O_3 which were neglected in the estimation.

B. *Estimation of the AlN.*—The method used was the decomposition of the nitride by HCl and the estimation volumetrically of the amount of NH_3 produced. A weighed quantity of the powdered substance was heated in a flask with HCl, as in 2 A, for two to three hours; the flask (B) was then fitted up; excess of strong KOH solution was then run in through the funnel (D), and the evolved NH_3 collected in standard H_2SO_4 in C. It will be noticed that air free from ammonia is aspirated through the apparatus during the whole time of the distillation; this ensured a regular and steady ebullition in the flask A; a few drops of phenol-phthalein solution was always placed in B before fixing up in order to indicate when excess of KOH had been added. A contains dilute H_2SO_4. Flasks B and C were easily removed, and replaced without disturbing remainder of apparatus. Blank experiments were carried out with the apparatus as well as tests with known strengths of NH_4OH solution in order to test its accuracy.

Contents of Flask B.	Contents of Flask C.	Acid found in C after Distillation.
(1) 100 c.c. conc. KOH.	10 c.c. $N \cdot H_2SO_4$.	10 c.c. $N \cdot H_2SO_4$.
(2) 50 c.c. conc. KOH.	20 c.c. $N \cdot H_2SO_4$.	20 c.c. $N \cdot H_2SO_4$.
(3) 5 c.c. $\frac{N}{10} \cdot NH_4OH$ and excess KOH.	5 c.c. $N \cdot H_2SO_4$.	45 c.c. $\frac{N}{10} H_2SO_4$.
(4) 5 c.c. $\frac{N}{10} NH_4OH$ and excess KOH.	10 c.c. $N \cdot H_2SO_4$.	95 c.c. $\frac{N}{10} H_2SO_4$.

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METHOD OF CALCULATING COMPOSITION OF PRODUCT.

(1) By direct estimation is obtained weight of Al, C, and AlN.

(2) By direct estimation is obtained weight of Al_2O_3 produced from Al, AlN and Al_4C_3, and Al_2O_3.

(3) Let X be weight of substance taken and
Let X^1 be weight of (Al + C + AlN) found.
Then $X - X^1$ is weight of Al_4C_3 and Al_2O_3 in original substance.
Let x be weight of Al_2O_3 found by experiment produced from Al, AlN, Al_4C_3 and Al_2O_3,
And y be calculated weight of Al_2O_3 produced from X^1 parts of (Al + C + AlN);
Then x-y is the weight of Al_2O_3 produced from $(X - X^1)$ parts of (Al_4C_3 and Al_2O_3).
When Al_4C_3 (144) is converted into $\longrightarrow 2Al_2O_3$ (204), an increase of 60 parts by weight corresponds to 144 Al_4C_3.
Hence an increase of $[(X - X^1) \sim (x-y)]$ parts by weight corresponds to $\frac{144[(X - X^1) \sim (x-y)]}{60}$ parts of Al_4C_3 (say $= Z$), and hence also weight of $Al_2O_3 = (X - X^1) - Z$.

Note on the Solubility of Al_2O_3 in HCl.—Statements as to the solubility of Al_2O_3 in HCl differ considerably. As in our method of analysis we wished for confirmatory evidence as to the solubility of Al_2O_3 under the conditions there carried out, the following tests were performed:

Test 1.—Anhydrous Al_2Cl_6 was heated in the muffle furnace at a temperature of 1,000° — 1,100° C. for five hours, thus converting it into Al_2O_3. A weighed quantity of this Al_2O_3 was boiled for three hours with conc. HCl, allowed to stand three hours, filtered and residue well washed, &c. The Al in filtrate was estimated by NH_4OH in usual manner:

Weight of Al_2O_3 used	2·4085 grms.
Weight of insol. portion in HCl ...	0·6900 „
Weight of soluble	1·7026 „
Total	2·3926 „

Test 2.—A layer of Al powder (purified) about $\frac{1}{8}$ in. deep was spread over a porcelain basin and inserted into the hottest part of the muffle, which was left open. The Al commenced to burn and was brought to the front of the muffle, and here continued to burn with intense light and heat. The residue was greyish-white, not pure white, whilst a fairly large amount of black substance was present. This was boiled for three hours with 2 N · HCl to remove any nitride * and free Al, and after drying a weighed amount was then boiled with conc. HCl for three hours.

Weight of Al_2O_3 used	1·9300 grms.
Weight of Al_2O_3 insoluble ...	1·3845 „

Pionchon † showed that the grey powder was probably Al_6O_7 or $Al_2O \cdot 3\,Al_2O_3$. Duboin ‡ showed that the grey powder was not a mixture of Al_2O_3 and Al, because on mixing Al_2O_3 and 4 Al and heating a vigorous action takes place.

* See analysis of nitride in Al powder burnt in air.
† *C. R.*, 117,328–117,330. ‡ *C. R.*, cxxxii., No. 13.

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Test 3.—A portion of the slag from a Goldschmidt's reduction of Fe_2O_3, after grinding to pass a 40,000-mesh sieve, was boiled with conc. HCl for six hours and nine hours respectively:

Weight of slag used	4·3800 grms.
Weight of insol. matter after six hours ...	2·2632 „
Weight of insol. matter after nine hours	1·9010 „

The filtrate in each case contained Al and Fe.

Conclusion.—It is evident that strongly heated Al_2O_3 is slowly attacked by conc. HCl, and hence in the method of determining constitution of products obtained from Al_4C_3 some of the Al_2O_3 went into solution on boiling with the HCl, as was found by the calculation of results.

The content of Al_4C_3 in the product could have been estimated by determining the volume of CH_4 evolved by the action of water in HCl, but this method was not adopted for two reasons. First, the action of water was extremely slow (1 grm. of the well-powdered substance slowly produced gas for a week and even then the action was incomplete); secondly, even on using dilute HCl, the evolution of gas was slow and protracted owing to the protecting layer of Al_2O_3 present; hence the method adopted was the one described.

Analysis of the Gas evolved by Action of Water and Hydrochloric Acid.—No attempt was made to determine the quantity of gas evolved from known amounts of the solid for the reasons just given, but the gas evolved from different samples, and different portions of the same crucible were carefully examined, with a view to throwing light upon the nature of the carbides present. The samples were placed in small Bohemian flasks (300 c.c.), having a side tube in the neck, and connected to a Winchester quart bottle filled with water, which acted as an aspirator gas-holder; the flask was filled with distilled water, and a well-fitting cork inserted into the neck, care being taken to exclude air. The apparatus was then put by and allowed to remain for intervals of time extending from one day to sixteen weeks.

Hempel's technical gas apparatus was used for estimating the constituents of the gas evolved, all the solvents and the containing water in the measuring and pressure burettes being well shaken with the various samples before making observations. Each sample was tested for CO_2, CO, O, and unsaturated hydrocarbons, but in no case was any of these gases found. The saturated hydrocarbons and hydrogen were then determined by taking a known volume of the gas, mixing it with a known excess of air, and exploding over water in a Hempel's explosive pipette, measuring diminution in volume, absorbing CO_2 produced and measuring its volume, passing residual gas into alkaline pyrogallic acid, and measuring the volume of O thus absorbed. In order to check this work some half-dozen samples of the gas were likewise analysed in Dr. Bone's apparatus for exact gas analysis over Hg, and the results so obtained did not differ by 1 per cent. from the results obtained with Hempel's apparatus. From the diminution in volume after explosion of the volume of CO_2 formed and the volume of O used in explosion it was deduced that the explosive gas was a mixture of CH_4 and H. In all experiments a gas residue was obtained, which could only be put down as N, and for some time it was a matter of speculation as to the source of this N. Explosions with pure O were carried out, and still the same percentage of residue (N) was obtained. It was, however, noticed that the percentage of N was greater in those samples which had been standing for some time; in fact, those gases which were analysed within twenty-four hours of their starting contained less than 2 per cent., whereas one that had stood three months contained 8 per cent.

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It was then thought that the N came from the dissolved air in the water used. An active sample of powdered material was therefore treated with water in the apparatus described and the gas analysed at end of known intervals of time in Dr. Bone's apparatus, with the following results:

At end of twenty hours	$CH_4 = 43{\cdot}8$	$H = 52{\cdot}0$	$N = 4{\cdot}2$
At end of three days	$CH_4 = 43{\cdot}0$	$H = 51{\cdot}0$	$N = 6{\cdot}0$
At end of seven days	$CH_4 = 42{\cdot}5$	$H = 50{\cdot}3$	$N = 7{\cdot}2$
At end of fourteen days	$CH_4 = 42{\cdot}4$	$H = 50{\cdot}1$	$N = 7{\cdot}5$

It will thus be seen that the explanation suggested is the correct one.*

At first the presence of H in the evolved gases was inexplicable, but when the large amounts of nitride were noticed the explanation was evident. The nitride is slowly decomposed by the water producing NH_3, viz., $AlN + 3H_2O = Al(OH)_3 + NH_3$. This NH_3 in the presence of water is acted upon by the finely divided Al, similarly to the action of NaOH in Al, with the evolution of H.† To test this hypothesis some of the purified Al powder was placed in the gas-generating apparatus and treated with NH_4OH solution; gas was slowly evolved, and in twelve hours over 200 c.c. had been collected, which proved to be nearly pure H (about 2 per cent. of N was present from the same cause as before).

ANALYSES.

Sample.		Percentages. Free C.	Free Al.	AlN.	Al_4C.	Al_2O_3.
A. 4 *Al* + 3 *C*.						
1. Made in open crucible	Top layer ...	3·3	2·9	22·65	42·09	29·06
	Bottom layer	4·8	2·8	22·83	53·34	16·23
2. Made in closed crucible and heated 2 hours	Top layer ...	8·09	1·07	11·84	23·46	55·54
	Bottom layer	7·96	1·40	16·87	36·11	37·66
B. 8 *Al* + 3 *C*. Middle portion containing blue and yellow crystals ...		2·29	0·5	40·37	9·12	47·72
C. 4 *Al* + 6 *C*. Lower layer		20·1	0·25	3·67	65·91	11·07

Analyses of Gas.

The following analysis is typical of the method used throughout when using Hempel's apparatus:

* That the residual gas was N was confirmed by (*a*) sparking with O over KOH solution, (*b*) spectroscopic investigation.

† About 6 grains of purified Al was placed in distilled water in the generating flask, &c., and at the end of two months not more than 1 c.c. of gas had been evolved—this probably came from traces of Fe.

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Volume of gas taken = 100 c.c.
Volume after passing into KOH pipette = 100·0 c.c. CO_2 = 0·0 c.c.
Volume after passing into P pipette = 100·0 cc. O = 0·0 c.c.
Volume after passing into Br pipette and then into KOH pipette = 100·0 c.c. Unsaturated hydrocarbon = 0·0 c.c.
Volume after passing into acid Cu_2Cl_2 pipette = 100·0 c·c. CO = 0·0 c.c.
Gas passed into P pipette and a sample of it taken for explosion:
Sample taken = 8·3 c.c.
Volume sample and air = 99·8 c.c.
Volume of air = 91·5 c.c.
Volume after explosion = 85·0 c.c.
Diminution in volume = 14·8 c.c.
Volume after passing into KOH = 78·5 c.c.
Volume of CO_2 = 6·5 c.c.
Volume after passing into P = 73·8 c.c.
Volume of O left = 4·7 c.c.
Volume of CH_4 = volume of CO_2 = 6·5 c.c.
Diminution due to CH_4 = 2 × 6·5 = 13·0 c.c.
Hence volume of H = $\frac{2}{3}$(14·8 − 13·0) = $\frac{2}{3}$ × 1·8 = 1·2 c.c.
Hence volume of N = 8·3 − (6·5 + 1·2) = 0·6 c.c.
Actual volume of O taken = $\frac{1}{5}$ × 91·5 = 18·3 c.c. (approximate).
Volume of O used = (2 × 6·5) + ($\frac{1}{2}$ × 1·2) = 13 × 0·6 = 13·6 c.c.
Hence volume of O should = 4·9 c.c.
Actual volume found = 4·7 c.c.
Composition of gas = 78·3 per cent. CH_4, 14·4 per cent. H, 7·3 per cent. N.

Other samples gave:

(1) Analysed twelve hours after commencement, 78·6 per cent. CH_4, 19·1 per cent. H, 2·3 per cent. N.

(2) Analysed three weeks after commencement, 75·0 per cent. CH_4, 18·1 per cent. H, 6·9 per cent. N.

Series II.

Aluminium Powder and Sugar Charcoal.

The sugar carbon was made from white lump sugar by heating small portions at a time in a cylindrical tin and finally heating in the muffle to 1,000°–1,100° C. It was well crushed on cooling, powdered and sifted through 40,000-mesh sieve; it was a bright, shiny powder, hard and difficult to crush, and it did not seem at all porous. The percentage of ash was zero.

Mixtures 4 *Al* + 3 *C*.—The interaction was tried in four ways.

Method 1.—Mixture was placed in a Hessian crucible and embedded in sand, so that the crucible could be covered with a beaker and air excluded. The action was started with a fuse and spread slowly over the top, but on covering over with a beaker it ceased. This was found to be the case on repeating several times. The reaction proceeded when left uncovered. It thus appears that the reaction between the Al and C requires a high initial temperature, and this is supplied by the burning C and Al in contact with the air.

Method 2.—Some of the mixture was placed in a $\frac{3}{8}$ in. test tube and the top drawn out to a fine capillary tube. The mixture was then heated till red hot, but no apparent change occurred, even after the whole of the mixture was red hot. On examination the

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Al powder was quite visible and the mixture appeared unchanged. Only a very slight evolution of gas was obtained by allowing the mixture to stand over water all night. It is evident that sugar carbon in this state of fineness, and with air excluded, does not combine with Al at a red heat.

Method 3.—Some of the mixture was heated in an open porcelain crucible over a Bunsen burner. The mixture slowly burnt at the surface and finally became incandescent. The mixture was entirely changed, no Al being visible, and a gas was slowly evolved on treating some of it with water.

Method 4.—A sample was placed in a Hessian crucible and covered as in previous experiments. It was heated in the muffle for two hours at 1,000°–1,100° C. On removal and cooling the contents were found to be solid, no Al was visible, and the core consisted of a mass of yellowish crystals.

The reaction between sugar carbon and aluminium powder is not nearly so striking as that between wood charcoal and Al, due probably to (1) the superior hardness and compactness of the sugar charcoal; (2) the non-porosity of the carbon preventing the occlusion of air; (3) the powder not being in such a finely divided state; and (4) the absence of possible helpful impurities, *e.g.*, Fe_2O_3.

Mixtures $4\,Al + 8\,C$.—This mixture could not be made to react in the cold, but on placing in the muffle reaction action started, and on withdrawing and cooling a sample of carbide was obtained which reacted with water most vigorously. Samples were therefore made by heating mixture in closed crucible for half an hour. The resulting product was quite soft and black, with patches of yellow crystalline masses.

Mixtures of $8\,Al + 3\,C$.—This mixture would not react in the cold, but did so easily in the muffle. Samples were therefore made as above. The resulting mass was found to be very hard and extremely difficult to remove.

ANALYSES.

SAMPLE.	PERCENTAGES.				
	Free C.	Free Al.	AlN.	Al_4C_3.	Al_2O_3.
A.—$4\,Al + 3\,C$—					
Top layer ...	9·04	1·00	13·93	24·78	52·25
Middle layer	9·57	1·75	18·05	34·39	36·24
Lower layer...	9·25	1·75	40·59	20·05	28·36
B.—$4\,Al + 6\,C$ ...	25·05	1·00	15·04	27·74	31·22
C.—$8\,Al + 3\,C$ ...	6·08	3·62	24·68	46·18	19·44

Analyses of Gas.

Sample 1—77·9 per cent. CH_4, 18·0 per cent. H, 4·1 per cent. N.
Sample 2—79·6 per cent. CH_4, 17·5 per cent. H, 2·9 per cent. N.
Sample 3—75·9 per cent. CH_4, 18·3 per cent. H, 5·8 per cent. N.

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Series III.

Aluminium Powder and Graphite.

Commercial graphite was used, which was found to be very impure and to react readily with Al powder in the cold. On igniting the commercial substance a brown ash was left which amounted to 50·1 per cent. of substance taken.

Boiling for twelve hours with conc. HCl gave a product which still yielded 47·3 per cent. of ash on ignition. The graphite obtained by treatment with conc. HCl was boiled for six hours with HF, and after this still yielded an ash of 15 per cent.

The partially purified graphite was now treated in an iron tray with fused NaOH for three hours, extracted with water, filtered, digested with conc. HCl, filtered, washed, and dried; after this treatment the ash was less than 1 per cent.

It was found that the original graphite could be purified by two successive fusions with NaOH. During the fusion H was evolved.

None of the mixtures of graphite and aluminium would react in the cold, but those in the proportion 4 Al to 3 C reacted with a fuse when heated to about 300° C. The action was brought about in each case by heating in the muffle, but the action was not so complete and vigorous as with the other forms of C.

The mixture 8Al + 3C gave a solid mass containing a yellow* crystalline portion. This yellow crystalline formation was seen more or less in all the samples.

Analyses.

Sample.	Percentages.				
	Free C.	Free Al.	AlN.	Al_4C_3.	Al_2O_3.
A.—4 Al + 3 C (yellow crys.)	15·2	0·25	20·04	10·68	53·83*
B.—4 Al + 6 C	26·78	0·5	17·52	33·69	21·51
C.—8 Al + 3 C	07·95	2·3	42·16	36·58	11·11

Gas Analyses.

1. Sample taken 1½ hours after starting:

80·9 per cent. CH_4, 16·9 per cent. H, 2·2 per cent. N.

2. Another sample 1 hour after:

77·1 per cent. CH_4, 21·8 per cent. H, 1·1 per cent. N.

Series IV.

Some experiments were carried out to see the influence of the air and of N in the combination of Al and C under the conditions already described. The mixture of 4 Al + 3 C (wood charcoal) were used.

* Dr. Seligman (*Trans.* Faraday Society, vol. iii., p. 177) calls attention to the existence of yellow crystals in the mass produced when Al burns in air, and suggests that they are crystals of Al_2O_3; the authors find that the yellow crystalline portions of their products are always high in Al_2O_3.

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1. *Heated in a Current of Air.*—Reaction proceeded before tube was visibly hot and proceeded vigorously. Product contained a very large amount of Al_2O_3 and 1·35 per cent. of AlN.

2. *Heated in a Current of N in Glass.*—Mixture was heated to dull redness, no visible action was seen. The product contained large amount of free C and Al and 3·517 per cent. AlN.

3. *Heated in Current of N in Berlin Porcelain Tube.*—The tube was heated to full red heat. Reaction took place to a greater extent than in 2. Product contained 10·46 per cent. AlN.

4. *Mixture Heated in vacuo.*—The mixture was placed in a piece of steel bicycle tubing and connected to a Topler pump. A very slight leak occurred at the joint between the glass and the steel tube, and it was probably due to the small amount of air thus left (the pressure was less than 2 cms. during the heating) that action took place. The tube was heated in a small Fletcher furnace to a bright red heat for twenty minutes.

The product appeared almost unchanged, and where the powder had agglomerated portions were picked put, ground up, sieved, and analysed.

The analysis gave :

Free C 23·44 per cent., Free Al 65·01 per cent., AlN 1·6 per cent., Al_2O_3 7·0 per cent., Al_4C_3 2·95 per cent.

The authors are of opinion that if air had been rigorously excluded very little action would have taken place. They hope to repeat this experiment.

NOTE.

Action of Magnesium and Carbon

Some experiments have been carried out on the direct combination of Mg and C, and evidence has been obtained, which the authors are now confirming, that a carbide of magnesium is produced under similar conditions to those described for Al and C.

CHEMICAL LABORATORY,
THE POLYTECHNIC,
REGENT STREET, W.
April 8, 1908.

DISCUSSION.

Dr. Richard Seligman (*communicated*): I am much interested in this Paper, which forms a continuation to the authors' previous careful work on the Goldschmidt reaction.

The authors have reached the conclusion that carbon and aluminium unite directly, and that it is not necessary for the intermediate formation of carbon monoxide to take place. In this view I quite concur. I have often found aluminium carbide formed in parts of the electric furnaces to which air could scarcely find access.

I am naturally interested in the conclusions which the authors arrive at with regard to the part which the combustion of aluminium in air plays in this type of reaction. By their well-conceived experiments (Series IV.) on the influence of air and nitrogen, the authors have obtained very striking confirmation of the view I put forward (this Journal, vol. iii., p. 177) on this subject.

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With regard to the formation of aluminium nitride, the authors have also found the opinion I expressed (*loc. cit.*) justified.

May I call attention to a slip in the authors' footnote on page 70. I did not suggest that the crystals found in the mass resulting from the combustion of aluminium were crystallised alumina. I stated this fact quite definitely. I am glad to see that the authors have confirmed this observation.

The authors describe a method of purifying graphite very similar to one which, unknown to them, has been used by Grossman. The process was worked on a semi-commercial scale in Manchester, but, so far as I am aware, has never been thoroughly developed. I gather that the evolution of hydrogen to which the authors draw attention was not noticed by Grossman or his co-workers. Was it not due to the iron disk?

Dr. F. Mollwo Perkin was not quite in favour of the suggestion that the reaction was initiated by oxidation of the carbon to CO and CO_2 and subsequent reduction of these gases. There was no evidence that at 1100° C CO could be reduced. The initial reaction was more likely to be superficial oxidation of the aluminium. The heat set up by the action of nitrogen on the aluminium might also help. The oxygen of the air alone might not oxidise the aluminium already superficially coated with oxygen, but the finely divided and intimately mixed carbon and the oxygen might together cause reaction to take place with the oxygen—at the temperature of the experiment. The temperature of the mass might then be raised sufficiently high to cause reaction between the aluminium and carbon to take place. It would be interesting to heat aluminium powder in a stream of CO and CO_2 and see at what temperature reduction did take place. He supposed every precaution had been taken to keep away grease.

Mr. Charles Weiss asked what the temperature was in the experiment of Fichter, quoted on the first page of the Paper. He had frequently found aluminium carbides at the bottom of aluminium furnaces, and as a rule these carbides were found to be entirely enclosed in an alumina coating. They consisted of bright yellow crystals which, when in contact with moisture, emitted a smell like acetylene. It was interesting to note (see footnote on p. 70) that Dr. Seligman referred to yellow crystals supposed to be Al_2O_3.

Perhaps the authors could get some further information regarding this matter from aluminium manufacturers.

Mr. W. E. Harris asked whether artificial graphite had also been tried by the authors in their experiments.

Mr. H. R. Ellis said that the nitride produced was probably due either to the action of nitrogen at a high temperature on the carbide or formed by the nitrogen combining direct with the aluminium owing to the presence of carbon. The former view was more probable, as it has been shown by several workers that the aluminium carbide is readily attacked by nitrogen at high temperatures.

The formation of nitride of aluminium by this method is the subject of two patents at least; the first, by Willson (21,755 of 1895), describes the formation of nitride by heating alumina and carbon in the electric furnace in a current of nitrogen. The second is by Dr. C. Serpek, of Luterback (13,579 of 1906).

Crude aluminium carbide, on heating strongly in a current of nitrogen, readily absorbs nitrogen, which is evolved as ammonia on treatment with water; for the successful absorption of nitrogen certain impurities are necessary. Now, aluminium carbide can be prepared in a crude state by

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simply heating clay and carbon in the electric furnace, and since this carbide would be very suitable for absorbing nitrogen, it seems quite possible that aluminium carbide could be used to absorb atmospheric nitrogen as successfully as calcium carbide is used for preparing the well-known cyanamide manures.

Professor A. K. Huntington was inclined to agree with Dr. Perkin that the oxidation of aluminium started the reaction. Perhaps, however, the action was a triple one, or perhaps it was brought about by the presence of a gas (CO_2 or CO) between two solids which would not react alone. It was frequently difficult to get reaction to take place between solids, and possibly the gas, unlike the carbon, might be able to permeate the film of oxide surrounding the aluminium, getting at the actual metal, and so start the reaction.

He expressed his appreciation of the great care with which the experiments had been made, and of the value of such carefully recorded work.

Mr. H. E. Weston, in reply, said that all grease had been carefully removed from the aluminium powder. With regard to Dr. Perkin's remarks he felt sure that the first action was the oxidation of carbon. This was evident from the appearance of the reaction, which started with a dull red heat below the surface, after which—but not at once—bright incandescence appeared on top. CO was undoubtedly produced, because in some of the experiments where the crucible had cracked the blue CO flame was clearly visible. Moreover Al powder heated in an open basin in the air, under conditions similar to those for heating a mixture of Al and wood carbon, did not burn even after the lapse of an hour.

The experiments described under Series IV. in the Paper also pointed to the initial action being due to the oxidation of the carbon.

As regards formation of nitride, to get any considerable yield of this it was necessary to have carbide present.

Artificial graphite was not used in any of the experiments, as the authors had no information with respect to the purity of the same.

The authors are pleased to rectify their statement as to Dr. Seligman suggesting that the crystals found in the fused aluminium being Al_2O_3, and note that he does definitely state them to be such. With regard to the evolution of H in the purification of graphite by fused caustic soda, the authors find that the gas does not come from the action of the fused NaOH on the iron, since the same inflammable gas is copiously evolved in carrying out the fusion in a platinum basin.

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TECHNICAL ELECTROCHEMISTRY IN RUSSIA.

By Professor N. PILTSCHIKOFF.

A Paper read before the Faraday Society, Tuesday, April 28, 1908, Professor A. K. Huntington, Vice-President, in the Chair.)

Before describing any new methods it is necessary that the notes of J. B. C. Kershaw* on the electrochemical works in Russia should be amplified. Besides the three works mentioned by Mr. Kershaw which prepare caustic soda and bleaching powder, viz., Lubimoff, Solvay & Cie, Zabkowickie Electrochemical Cie, and the Russian "Elektron" Company, there are several copper-refining factories, viz., that of the Siemens Company at Kalakant, which is not at present working, and a factory at Moscow which produces annually 500 tons of electrolytic copper, 1 ton of silver, and about 80 lbs. of gold; tin, nickel, and chromium are also prepared. There is also a similar factory at Petersburg, and equipment for the extraction of copper from its ores is erected at the "Medianke" mine at Boleslav.

At the latter place the method of Laschinsky (patented) is used. According to his observations the salts of iron, even in small quantities, are oxidised at the anode to a sulphate very rich in iron:

$$2FeSO_4 + H_2SO_4 + O = Fe(SO_4)_3 + H_2O.$$

This minimises the effect of the current and lowers the quality of the deposit. To avoid this oxidation the plates are covered with lead which forms the anode in the electrolytic bath, while the liquid is continually stirred. The effect of this arrangement is remarkable, the iron is no longer oxidised, and copper is deposited regularly in amounts up to 1·15 grms. per ampere-hour.

Several electrochemical methods are about to receive a technical application. Among these, the study of the electrical combustion of air made by Gorbov and Mitkievitch, professors in the Institut Polytechnique in Petersburg, may be cited. Their furnace (Fig. 1) consists of a chamber *B*, whose upper part is formed by a funnel *K*, connected to a worm in which the products of combustion can be cooled. The arc is formed between carbon or metal electrodes C_1 and C_2, and fills the whole of the funnel.† A current of air draws the arc into the worm, in whose mouth is formed a "bunch of fire," through which all the air has necessarily to pass. It is then cooled in the worm which is placed in a bath A filled with water or oil, whose temperature is not allowed to exceed a certain limit.

Fig. 2 shows the operation of a Gorbov & Mitkievitch furnace with a 12-kw. arc. The abscissæ show the percentage volume of nitrous oxide obtained, while the ordinates are the weight of nitric acid in grammes per

* *Transactions* of the Faraday Society, July, 1907. John B. C. Kershaw, F.I.C., "The Present Position and Future Prospects of the Electrolytic Alkali and Bleach Industry."

† Continuous or alternating current can be used (three electrodes are required with the 3-phase system). The terminal voltage is from 1,000 to 3,000 and across the arc from 600 to 1,500.

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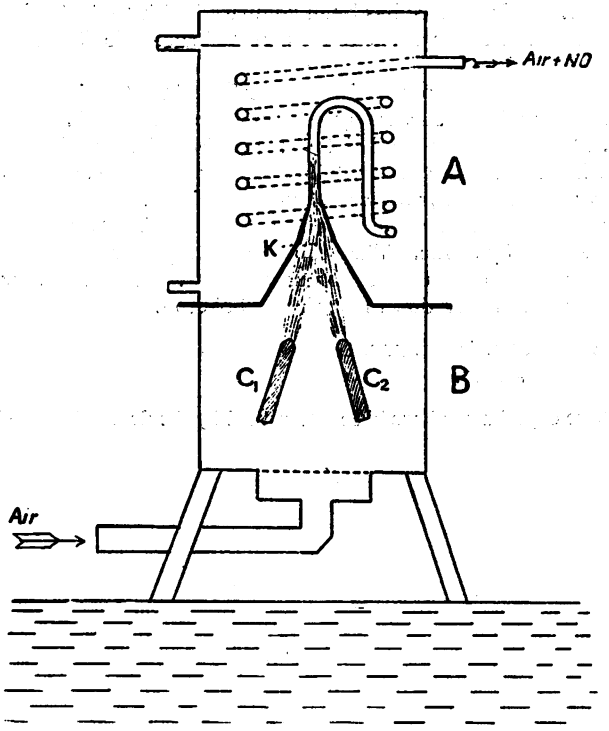

FIG. 1.—View of the Gorbov-Mitkievitch Furnace.

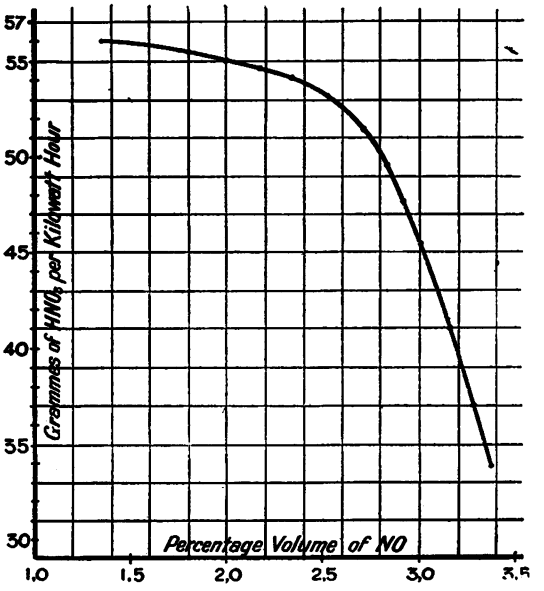

FIG. 2.—Operation of a 14-kw. Gorbov-Mitkievitch Furnace.

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kilowatt-hour. This furnace has been compared with that of Birkeland and Eyde, and is found to be much more economical, while its construction is simpler.

Professor Kloboukoff * of Kharkov has perfected the tanning of hides by the electric current which prevents any fermentation in the bath.

Dr. K. Danilevsky has studied the deposition of electrolytic copper on leather. The leather with its contained copper is harder, resists the action of lime to a greater extent, and wears out less quickly.

Successful experiments have been made at Petersburg on the Purification of various waters by ozone. The process is not yet widely used, probably for economical reasons. I have, however, seen at Moscow a very powerful and economical ozoniser due to Professor Sokotoff.

THE TECHNICAL INSTITUTE,
KHARKOV.

* These experiments have been interrupted by the death of Kloboukoff.

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REVIEWS OF BOOKS.

Thermodynamics of Technical Gas Reactions. F. HABER. Translated by ARTHUR B. LAMB. (London, 1908: Longmans, Green, & Co., 39, Paternoster Row, E.C. Pp. 356. Price 10s. 6d. net.)

The present work is an excellent English translation of Haber's lectures on the thermodynamics of technical gas reactions, which appeared in 1905. For the purposes of this translation, however, the original German edition has been brought thoroughly up to date. As is already well known, Professor Haber's work is a most notable contribution to a highly important subject. Indeed, it is not going too far to say that it is a pioneer monograph of the very first importance. Twenty years ago Le Chatelier, in discussing the variation of the equilibrium-constant of a gas reaction with temperature, drew attention to the importance of knowing how the specific heats of gases vary with temperature over wide ranges, and emphasised the necessity of determining the value of the undetermined integration-constant which appears in the integral equation expressing K (the equilibrium-constant) as a function of temperature and calometric constants. From the purely scientific standpoint Professor Haber's book has been written with the express purpose of dealing with these fundamental problems. With this object in view, his work forms a most excellent treatise on the thermodynamics of gas reactions, dealing with the subject *ab initio* and in the most thorough and interesting manner. Before the appearance of Haber's book both these cardinal points, viz., the variation of the specific heats of the interacting gases and the value of the undetermined integration-constant, had received but scant attention in works dealing with thermodynamics and physical chemistry. In order, however, to predict the course of gas-reactions over wide ranges of temperature (and especially at high temperatures) from data obtained at one or perhaps two temperatures, it is just these very points which require to be known.

Soon after the appearance of the first edition of Haber's work Nernst published important papers dealing with the question of the evaluation of the undetermined ("chemical") constant. An account of Nernst's theory is contained in the present translation. It will thus be seen that, viewed from the purely scientific standpoint, Professor Haber's work must take high rank as the classical treatise on the thermodynamics of gas reactions. In this respect there is nothing that can approach it in any language, and it can be most strongly recommended to every student of Chemistry and Physics. But Professor Haber's work must, although written in the most strictly scientific manner, appeal very strongly to engineers. As the title implies, the technical applications have been constantly kept in view. Now, although many branches of engineering have in recent years received fundamentally important advances from physical chemistry, and fuel-engineering not

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the least of these, it still remains a notorious fact that the great majority of trained engineers in this country are almost entirely ignorant of the principles of physical chemistry. It is to be hoped that Professor Haber's work, which includes in its scope the principles underlying the scientific study of water- and producer-gas manufacture, will do a great deal in this country towards removing this very unsatisfactory state of affairs. As for the chemical manufacturer and chemical engineer, who are already alive to the vital importance of physical chemistry, it may be safely said that they will derive the greatest possible benefit from a close study of the present work. Here they will find an exhaustive discussion of such technically interesting and important cases as the Deacon process, the contact sulphuric acid process, the formation of oxides of nitrogen from their constituent elements, &c. It is, however, not so much in its thorough grasp of the principles and details of known processes that Professor Haber's book may be expected to produce important results: the real benefit will be derived rather from the general principles and methods inculcated. A standard has now been set in the technical study of gas reactions which it is possible for others, provided they possess the necessary knowledge and training, to endeavour to attain.

Professor Haber deals with a host of related matters, amongst the most important of which are the methods of determining the specific heats of gases, high temperature measurements, the laws of radiation and the optical measurement of temperature, the E.M.F. of gas cells, &c. Those who are unfamiliar with the present state of this subject will be astonished to find that from E.M.F. measurements made at ordinary room temperatures, combined with the necessary calorimetric and specific heat data, successful calculation can be made of the direction and output of gas reactions at temperatures which are one or two thousand degrees higher.

Enough has been said to show that this work of Professor Haber's presents us with one of the best examples of how scientific theory can and must be applied to technical practice.

It only remains for the reviewer to recommend it most strongly to every one who takes an interest in the subject, whether he be manufacturing chemist, engineer, or college student. Those who have to teach the subject of thermodynamics will find in it a rich store of material wherewith to enliven their lectures and interest their students.

A Treatise on Chemistry. By SIR H. E. ROSCOE, F.R.S. and C. SCHORLEMMER, F.R.S. Vol. I.: The Non-Metallic Elements. 3rd edition, 1905, pp. 931, 21s. net. 4th edition, 1907, pp. 1,435, 30s. net. (London: Messrs. Macmillan, Ltd., St. Martin Street, W.C.)

The revision of these standard volumes has been carried out in such a thorough manner as to replace them in a pre-eminent position among works of their class. Such rapid progress has been made in chemistry during the last decade that the previous volumes were, unfortunately, behind the times, and we heartily welcome our old friends, now quite up to date. The fascinating style which makes Roscoe's works such delightful reading is fully retained and the references are fuller than ever.

Vol. I. Some hundred and thirty pages are devoted to the general principles of the science, and the non-metallic elements are next dealt with in turn. The cyanogen compounds are fully dealt with down to the manufacture of calcium cyanamide. Very instructive chapters are devoted to the manu-

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facture of coal-gas, water-gas, carburetted-water-gas and acetylene. The volume concludes with chapters on helium, neon, argon, krypton, and xenon.

Vol. II. This volume now includes the subject of crystallography, which was formerly dealt with in Vol. I. Pages are devoted to the thermal and microscopical examination of alloys, illustrated by curves and photo-micrographs. The application of the spectroscope to chemical analysis is referred to and references given to Roscoe's admirable work on that subject.

Alkali manufactured by the Leblanc, cryolite, and ammonia processes is fully dealt with and many admirable illustrations are given. The Castner electrolytic process, now in successful operation at Weston Point, is also described.

Glass manufacture, copper refining, and iron and steel manufacture are treated fully, with analyses and illustrations.

The volume concludes with chapters on the radioactive elements, radium, actinium, thorium, and uranium.

Thermochemistry. By J. THOMSEN. Translated by MISS K. A. BURKE. Textbooks of Physical Chemistry. Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S. (London: 1908. Pp. xv. + 495. Price 10s. Longmans, Green & Co., Paternoster Row, E.C.)

From time to time textbooks upon thermochemistry have been published in which the subject is set forth in greater or less detail, some being intended simply for elementary students and others more as reference books. In all of these books one cannot help noticing the frequent references which are made to the work of Julius Thomsen, and the work done by him is always looked upon as being authoritative. Therefore it is with pleasure that one hails the advent of a translation of Thomsen's Danish work.

The book is mainly a description of research work carried out in Copenhagen, work which, of course, is well known, but which for the first time is obtained completely grouped together. Even if the book consisted simply and solely of the numerical numbers obtained in these researches, that alone would be a cause of satisfaction to students of physical chemistry, but the book before us is more than that. It commences with an Introduction upon the object of thermochemical research. This then broadens out into a description of the methods employed in thermochemical determinations. The calorimeter employed by Thomsen in his determinations is described, as is subsidiary apparatus required.

Chapter I. deals with forms and properties of aqueous solutions, commencing with the absorption of gases and solution of liquids and solids in water. Then we come to tables showing heats of absorption and of solution, first of gases, then of liquids, and then of solids. After giving a large number of numerical data the theoretical results are discussed.

Chapter II. treats of heats of solution of salts which are partially dehydrated, also their heats of hydration and their constitution. Thus the heat of solution of disodium hydrogen phosphate is a positive number, the heat of solution of the same salt with two molecules of water of crystallisation is — 390 cals, with seven molecules of water it is more than —11,000, and with twelve molecules greater than —22,000.

Chapter III. deals with the influence of the amount of water upon the heat of solution, and then leads up to the heat of dilution of aqueous solutions. The heat of neutralisation of acids follows, and the special calorimeter employed for determining these heats of neutralisation is described and

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sketched. Part II. is devoted to compounds of non-metals, the investigation methods being first described, and then the theoretical results.

Space does not permit us even to tabulate the contents of this very useful book, much less discuss it in detail, therefore we will just mention one or two of the leading points, such as the nature of chemical reactions regarded from the dynamical standpoint, the decomposition of oxides by means of chlorine and reductions by the aid of carbon or carbon monoxide. Part IV. treats of organic substances, and this, like the other parts of the book, is first of all treated of according to the methods of investigation, the numerical data and then the theoretical reasonings. Perhaps some of the author's reasonings hardly conform to our present-day theory, but nevertheless his arguments are always interesting.

The book will be of the very greatest value to all students of thermochemistry, and will be very useful to chemists in general as a book of reference. We therefore have the greatest pleasure in recommending it as being an important addition to the series of textbooks upon physical chemistry. And finally, we have pleasure in congratulating Miss Burke on the very able and efficient manner in which she has carried out the translation and the publishers for the way the book is published and generally got up.

Modern Views of Electricity. By Sir Oliver Lodge, D.Sc. LL.D., F.R.S. Third Edition, Revised. (London: Macmillan & Co., Ltd., St. Martin's Street, W.C. 1907. Pp. 518. Price 6s.)

A special interest always attaches to the successive editions and revisions of Lodge's "Modern Views." The chances are that it will always be more or less out of date (we speak quite comparatively, of course) before it has passed through the press, so rapidly is physical science advancing at the present day. How different are the conceptions concerning electricity which are prevalent now to those held in 1889, when the first edition of this book appeared! Then the whole scientific world was dazzled by the brilliant verification of Maxwell's electromagnetic theory which Hertz's experiments were the first positively to confirm, and attention being entirely concentrated on the medium which conveyed electromagnetic energy, the function of the metallic circuit, until then supposed to carry the "electric current," was almost entirely ignored. Now, thanks in great part to Maxwell's own successors, the electron theory holds complete sway over the electrical world, and there is even some fear that the part played by the medium may in its turn be forgotten, or at least temporarily overlooked. Sir Oliver Lodge, therefore, very rightly insists that it is impossible rightly to follow the newest researches without acquaintance with the long-established fundamental truths concerning electricity and magnetism in general, and he is careful to point out that not—to any extent—*alterations*, but merely *additions* are all that it has been necessary to make in order to bring the "Modern Views" of 1889 and 1892 in line with the "Modern Views" of 1907. The new discoveries supplement the old; they do not replace them, as some superficial and careless observers have supposed. This being the case, the third edition of "Modern Views" not only retains to the full all the charm and interest of its predecessors, but it has acquired in addition a new fascination and delight of its own. We can only say: Go—read it!

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Transactions
OF
The Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. IV. OCTOBER, 1908. PART 2.

THE INDUSTRIAL USES OF OZONE, PARTICULARLY FOR THE PURIFICATION OF WATER.

BY F. MOLLWO PERKIN, PH.D.

(*A Paper read before the Faraday Society, Tuesday, May* 12, 1908, Mr. LEON GASTER *in the Chair.*)

The formation of ozone by the discharge of an electrical machine was originally noticed by Van Marum in 1785, but it was Schönbein in 1840 who first actually prepared it and gave it the name "ozone," from the Greek meaning "smell." He also showed that it was much more active as an oxidising agent than ordinary oxygen. It is produced by the slow oxidation of phosphorus, and the peculiar smell of this element is really not the smell of phosphorus but the smell of ozone, and this can be shown to be the case by adding small quantities of substances to phosphorus which prevent its oxidation, when the smell is no longer perceptible. It also appears to be produced in small quantities by the burning of hydrocarbons. It is likewise formed in the open country, probably by slow evaporation or possibly by electronic action of the sun. Thus, where there are large quantities of water, as in the neighbourhood of the sea, the amount of ozone will probably be greater than in dry inland districts, although what is often at the seaside put down to the smell of ozone is simply the smell of decaying seaweed. It is formed in considerable quantities when fluorine acts upon water. If a drop of water is introduced into a tube filled with fluorine, reaction immediately ensues, and the tube becomes filled with deep blue vapour; this is ozone, which has a blue colour when concentrated—

$$3F_2 + 3H_2O = 6HF + O_3.$$

Ozone is also produced at the anode when acid solutions of water are electrolysed, particularly if the electrode is a platinum tube through which cold water is passed. Fischer and Massenez (*Zeit. f. anorg. Chem.*, 1907, 229) have obtained 25·27 per cent. of ozone in electrolytic oxygen by cooling to 0°; such a process would not however be satisfactory on a large scale. The best method to prepare it is to subject oxygen to the action of the silent electric

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discharge, the oxygen thereby receiving electrical energy and becoming converted into ozone, thus—

$$3O_2 + \text{energy} = 2O_3.$$

Consequently ozone is less stable than oxygen and is in a condition in which it will readily part with the energy originally received electrically in the form of heat—*e.g.*, when the pure gas explodes or as chemical energy when it oxidises substances. The thermochemical equation accounts for its instability.

$$O_2 + O = O_3 - 32{,}400 \text{ cal.}$$

Ozone is a blue gas—although when largely diluted with air this colour is not noticeable—which boils at −119°; it can therefore be obtained

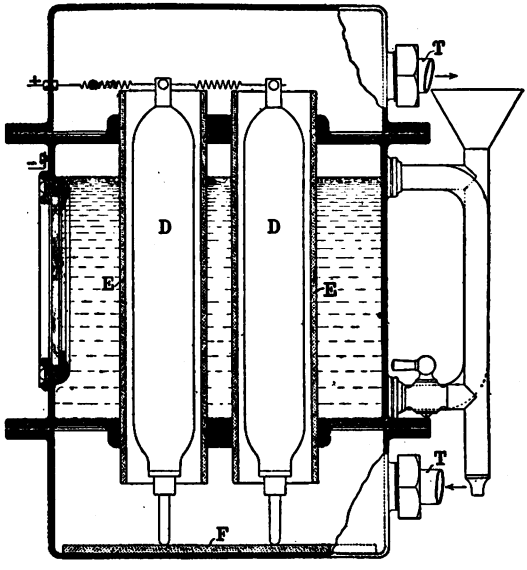

FIG. 1.

by passing ozonised oxygen through a tube surrounded by liquid oxygen (boiling point −182·5), a deep blue liquid being obtained. Its well-known sterilising properties are due to its great power of oxidation, and it is thus a very powerful bactericide. The employment of ozone or ozonised air for the purification of water on an industrial scale was suggested some years ago, but it is only within the last decade that the suggestion has been practically worked out and actually employed commercially.* Of all the workers on the subject Messrs. Siemens and Halske have been most indefatigable and have fitted up works at Paderborn and Wiesbaden, which have been in operation for some years and have given considerable satisfaction, particularly the former.

The providing of a pure water supply to our towns, cities, and villages is of the very first importance. In some cases where the water comes from sources in which contamination of the supply is out of the question, such as from mountain lakes or from deep springs, no special purification is

* Werner Siemens originally suggested its employment for this purpose in 1889, but the idea was put on one side, and not until 1898 was it again taken up by Messrs. Siemens and Halske.

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FIG. 2.

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necessary. In other cases, however, where the source of water admits of or even invites contamination purification in some way or other is a *sine quâ non*. The method chiefly employed is mechanical filtration. Chemical methods, such as treatment with oxidising agents, can only be carried out on a small scale. Electrolytic methods, although frequently tried and continually patented, have also proved not to be satisfactory, at any rate on a large scale. The sand filtration method is partly bacterial and partly one of filtration. The surface of the sand becomes coated with a slimy deposit, which is partially of bacterial formation; consequently the water first passes through the bacterial layer, which exerts a beneficial effect in destroying harmful bacteria, and also makes a much finer filter than can be produced by the more or less coarse-grained sand, and then it percolates through the sand. Sometimes, however, owing to floods and special contamination, the filter-bed system breaks down, and then it may be a very serious matter for the populace.

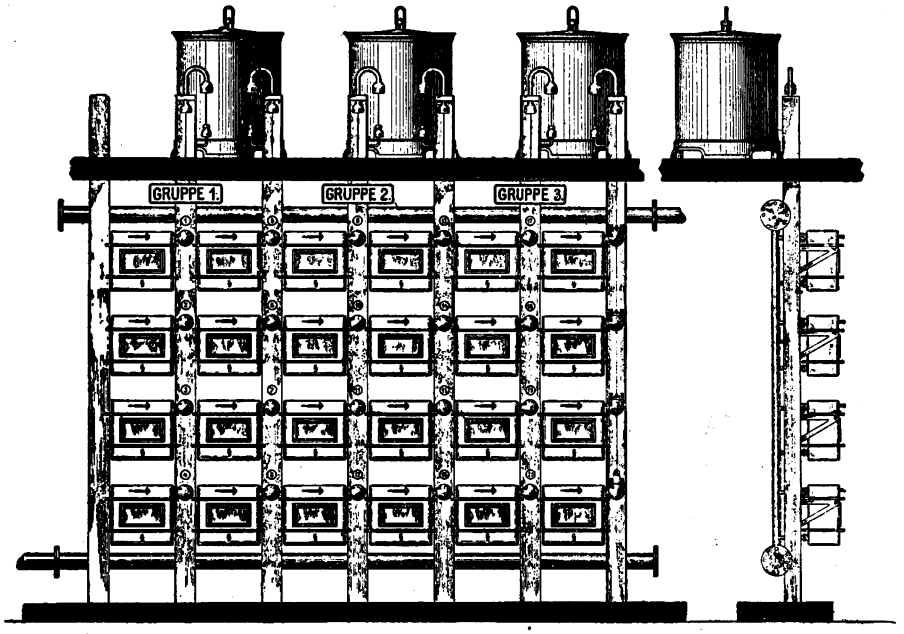

FIG. 3.—Battery of Ozonisers.

Purification by means of ozone may be said to be electrical, chemical, and mechanical. The electric current is required to produce the ozone, the ozone acts chemically upon the water, and the water is mechanically raised to high towers and allowed to trickle down over the layer of pebbles, where it meets the ozone: furthermore, it may be necessary or advisable to subject it to a previous filtration.

Dr. G. Erlwein having kindly supplied me with details of the Siemens-Halske process as it is carried out at Paderborn and Wiesbaden, I will describe the first of these installations, as it is typical of the plant which they are supplying, and has now been worked successfully for some years.

The ozoniser employed is shown in Fig. 1. It consists of concentric pipes *A* and *E* placed one within the other. The inner one is of aluminium, and is connected with the leads carrying a high-tension

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current, marked in the diagram as +, as this is the positive pole. As currents of the high voltage employed are very dangerous, the leading-in wires are very thoroughly insulated and are passed through the hollow hermetically sealed pillars, and the frame of the ozoniser. The glass cylinder *E* is the other pole; it is surrounded with water which can be circulated for cooling purposes, and as this is "alive" it receives its charge from it. The water which surrounds the glass cylinder receives its electricity from the iron-containing box, which is earthed, and consequently forms the negative pole. The annular space between *D* and *E* is where the silent discharge takes place. The complete apparatus consists of a cast-iron box divided into three chambers, the lower chamber for receiving and conveying the air to the ozone tubes, an hermetically sealed middle compartment into which the ozone tubes are inserted by means of a stuffing-box gland, and an upper compartment for collecting the ozonised air. Fig. 2 shows the apparatus as it appears closed up.

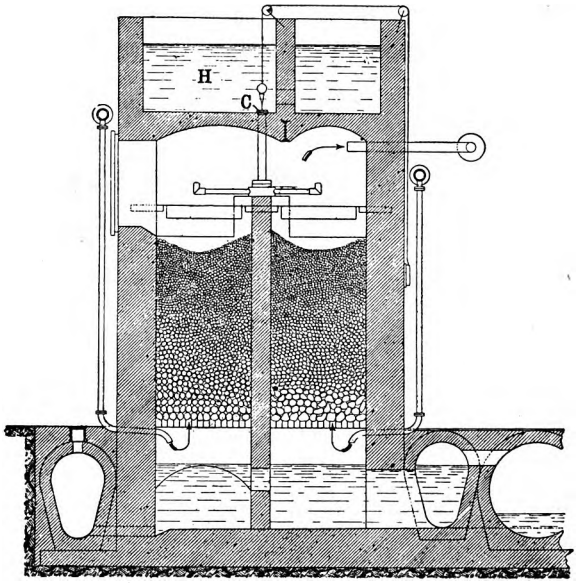

FIG. 4.

A plate-glass inspection window is fitted to each apparatus, so that it is easy to see whether it is functioning properly owing to the appearance of the blue discharge. The ozone-room in which the ozonisers are kept is usually dark to enable the attendant upon entering it to see at a glance whether they are working properly—*i.e.*, whether the apparatus has a uniform bluish glow. An ozoniser of this construction carries an alternating current having a potential of 8,000 volts; 1 h.p. per hour is required to operate it, and from 13·5 to 27 grm. of ozone is generated in that time, depending upon the amount of air which passes through the ozoniser and upon the degree to which it has been previously dried. The water at Paderborn and Wiesbaden requires an average consumption of 1·3 grm. of ozone per cubic metre (35·3 cubic ft.). Consequently, taking the daily consumption of water at 100 litres per head of population, each ozoniser is capable of sterilising water in twenty-four hours sufficient for a town of from 2,400 to 4,800 inhabitants. The figure 100 litres per head is probably rather low for this country,

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therefore it is perhaps better to put the capacity of the ozonisers as sufficient for from 2,000 to 4,000 inhabitants.

In the Paderborn works the installation consists of a battery of nine ozonisers, with two sterilisation towers erected outside the ozone chamber. The battery is made up of three independent sets, each consisting of three ozonisers arranged as shown in Fig. 3, which represents schematically the Paderborn plant.

One of the three sets is kept in reserve while the other two are used to supply the sterilisation towers. The towers are 4 metres (141·2 ft.) high; they are constructed of concrete and contain pebbles about the size of pigeon's eggs. Over these pebbles the water trickles and is therefore broken up into a number of small streams so that a very large surface is exposed to the action of the ozonised air, which is forced under a gentle pressure up the towers by means of blowers. Each complete tower, as shown in Fig. 4, is divided into three parts—(1) the reservoir *H* for containing the water to be treated, (2) the sterilising compartment containing the pebbles, (3) the receptacle for collecting the treated water. The interior of each tower is divided by means of two partitions into four independent towers, all of which obtain their water from a common supply pipe with a valve *C*. Every single tower or shaft is divided by a grating into an upper and lower part containing the pebbles 2 metres in thickness, and a lower reservoir for

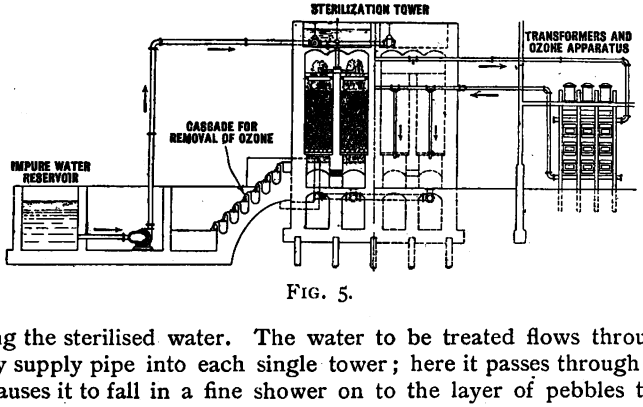

FIG. 5.

collecting the sterilised water. The water to be treated flows through the four-way supply pipe into each single tower; here it passes through a sieve which causes it to fall in a fine shower on to the layer of pebbles through which it percolates, becoming ozonised, and finally collects in the reservoir. Each of the single towers is one square metre in cross-section, and about 15–20 cubic metres (529–706 cubic feet) of air passes through it in the twenty-four hours. At the sides of the tower cascades are built over which the escaping water flows to the final storage reservoir. All traces of dissolved ozone are thus lost by the contact with the atmosphere. The scrubber system is found to give better results than can be obtained by forcing ozonised air up through a large bulk of water, because, the water being in very thin layers as it percolates through the pebbles, a much larger surface is exposed to the action of the ozonised air than can be the case when the air is forced up in individual bubbles.

In case of interruption either to the electric supply or to the blowers arrangements have been made by means of which the water is automatically shut off from the sterilising towers, thus preventing the inflow of unsterilised water into the town mains. For instance, if the current in one set of ozonisers be interrupted, thus stopping the ozone formation, a lever in connection with the electromagnet which is held in place by the passage of

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the current drops and closes an independent circuit, which in turn by electromagnetic action causes a floating conical rubber valve to drop and shut off the water supply to the four towers. On the other hand, should the blower break down, an aluminium disk which is inserted into the main air-pipe and kept raised by the pressure of the current of air as it passes under normal conditions drops, and likewise by electromagnetic action shuts off the water supply to the towers. In either case the fall of an indicator attached to the switch-board tells which set of apparatus is not working, and an alarm signal rings until the trouble is rectified; consequently it is not possible for the pure water to become contaminated with the unsterilised water. Fig. 5 illustrates the Paderborn water sterilisation plant.

The method just described is employed in cases where it is not required first to filter the water. Where the water contains suspended matter it is necessary to have a filtering plant in connection with the installation.

The plant at Wiesbaden is arranged upon practically the same plan as that at Paderborn, and is constructed to treat 250 cubic metres (882·5 cubic ft.) of water per hour, which is obtained from springs situated near Schierstein, along a former arm of the Rhine. The plant is in duplicate, each part being capable of dealing with 125 cubic metres (451·25 cubic ft.) per hour, but as a rule only half the plant is in operation at one time, thus giving a reserve of 100 per cent. Messrs. Siemens & Halske, besides fitting up large ozone plant, also build smaller laboratory and experimental apparatus to deal with small quantities of water, which can either be used for purifying water on the experimental scale or might be used for oxidation of chemical products, and they are also suitable for use in dwellings or restaurants, &c. They have also shown their versatility by inventing and fitting up transportable apparatus which could either be used in war-time or for dealing with contaminated water supplies; and one has only to remember the terrible mortality from enteric fever which ensued in the Transvaal War to realise the importance of such a means of purifying water in camp and upon the battle-field, where ordinary filtering appliances would be useless and it is not always feasible to boil large quantities of water. The apparatus consists of two small wagons, each of which is hauled by one horse. The small dynamo and all the pumping appliances are worked by means of a petrol motor. This apparatus was employed in the recent Russo-Japanese War and gave the utmost satisfaction. Other cases where a portable steriliser might be of great use would be in cases of an epidemic where the water supply of towns or villages has become contaminated. It is not so very long ago that a terrible outbreak of typhoid took place in Maidstone, and it will be remembered how great was the mortality. The source of the typhoid was ultimately traced back to the contamination of the water supply, and it was some considerable time before this became sufficiently pure to be again employed. One might not like the idea of drinking water containing dead typhoid germs, but it is certainly better than drinking water containing live germs, and in the case of ozonisation pathogenic bacteria are very susceptible to the action of the ozone. The compended table shows how complete the sterilisation of water is after ozonisation, and it will be noticed that where germs remain in the water they are of a harmless nature and non-pathogenic. The tables given only include a few cases, but both in France and in Germany, where so much work has been done with ozonisation. Similar results have been obtained in numerous cases in this country and abroad.

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BACTERIOLOGICAL RESULTS.

Ozone Experimental Works, Martinkenfelde.

Number of Bacteria per Cubic Centimetre of Water.

Before Ozonisation.	After Treatment.	Source of Water.
53,500	0	River Spree
108,370	10	" "
110,147	2	" "

IMPERIAL HEALTH BUREAU (OHMULLER-PRALL).

Number before Ozonisation.	Number after Ozonisation.		Species of Bacteria	Source.
	Ordinary.	Pathogenic.		
38,330	8	0	Cholera.	Spree water infected with cholera.
16,590	9	0	Typhus.	Boiled water infected with typhus.

The operating costs are by no means high : at Paderborn only two men are required to look after the whole installation, so that the cost of labour is a comparatively small item. It is stated that a plant capable of treating two thousand cubic metres (70,640 cubic ft.) of water per hour requires 275 h.p., while 45½ h.p. is necessary for a plant capable of treating 200 cubic metres (7,064 cubic ft.) per hour. This works out at about 0·1d. for the larger plant and about ¼d. for the smaller plant. These numbers refer to steam plant ; if producer gas is employed the cost is slightly less. Of course the purity of the water to be treated also has a considerable bearing upon the cost. The purer it is in the initial stage the less ozone is required to purify it, whereas if the water were very impure the ozoniser would necessarily require to yield a product richer in ozone.

THE OTTO SYSTEM.

Another process which has been found to work very successfully upon a large scale for the purification of potable water is the Otto system. The

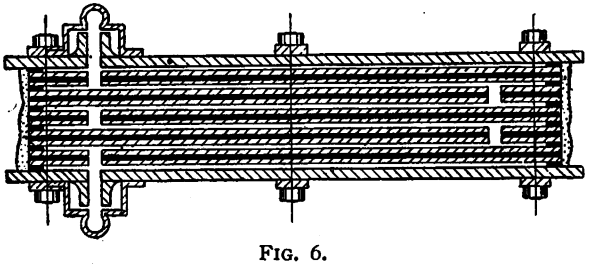

FIG. 6.

ozoniser itself consists of a series of transverse plates so arranged that a dielectric plate is placed between each electrode plate, the arrangement being electrode, dielectric electrode, and is shown diagrammatically in Fig. 6.

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The air is drawn or blown between the plates, the silent discharge passing between the spaces of the plates and thus ozonising the air or oxygen. There are an odd number of electrodes similar in arrangement to an accumulator, the odd and even being connected to separate poles of the source of current, the whole system being held in a frame.

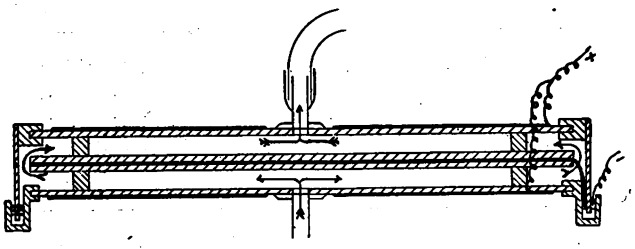

FIG. 7.

Fig. 7 gives an idea of the manner in which the air passes over the plates. The alternating current machine of particular design is employed and the best results are said to be obtained with a pressure of 6,500 volts, the current intensity being 0·00146 ampere. Under these conditions the apparatus can

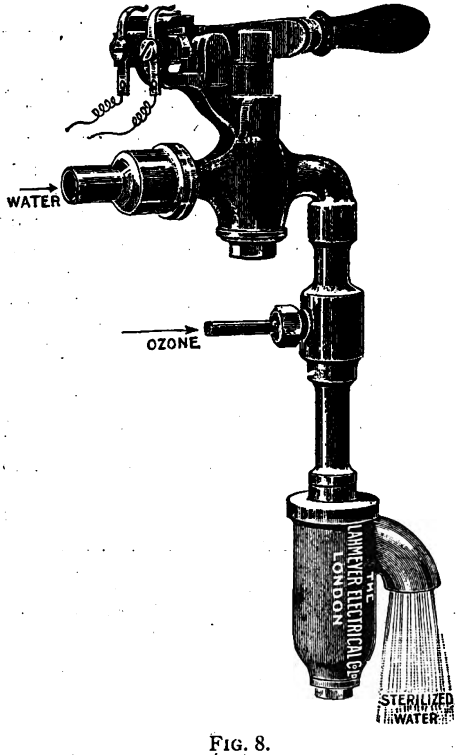

FIG. 8.

be used for hours without any appreciable warming taking place. The more rapidly the air is passed through the ozoniser, the better the yield of the ozone.

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Another form in which revolving electrodes are enclosed in a metal chamber which forms one pole, employs a current with a tension of about 25,000 volts, and is stated to be very efficient when large volumes of air have to be dealt with.

The Lahmeyer Electrical Company, Ltd., who are the agents in this country for the Otto process, have also a very useful little apparatus for the sterilisation of domestic water supplies. The ozoniser works directly on to the water supply, and is automatically set in action by turning on the tap. The apparatus is worked from an ordinary 16-c.p. lighting socket, and is designed for use upon 100 to 250 volt mains. If the current is alternating it is transformed up to 3,500–8,000 volts. If it is direct then a small motor converter is supplied with the apparatus.

Fig. 8 illustrates the manner in which the apparatus is connected with the water tap, and explains itself without further description.

Fig. 9 shows the whole apparatus fitted up ready for use. Recently a slight modification has been made in the apparatus by the fixing of a better "emulsifier" for mixing the ozone with the water, which is much more efficient than the one shown in the illustration. The whole apparatus, together with the transformer, does not occupy more than 1·25 square feet of wall space. Such an ozoniser is capable of sterilising 250 quarts of water per hour, which of course is much more than would be needed for ordinary domestic requirements. At the moment of being drawn off the water has a distinct smell of ozone, but if it be poured from a jug into a tumbler the smell will be noticed to have completely vanished and no taste of ozone can be noticed on drinking the water. At the same time, it is probably advisable to allow the water to stand ten minutes or so in order that there shall be no doubt about the complete absence of ozone. The ozone having done its work—that is, having sterilised the water—one does not desire to drink a disinfectant. As a matter of fact if the water is allowed to stand for ten minutes or is poured from the jug to the glass and back again and then again into the glass, no ozone remains, but the water contains slightly more free oxygen than ordinary water, and this is an advantage rather than a disadvantage. Over five hundred of these ozonisers have been installed by the French Government in Paris.

The Otto process, like the Siemens-Halske process, is also employed upon a very large scale for the sterilisation of water for towns and cities. At Nice an installation for treating 5,000,000 gallons per day has been in operation for about three years. The circuit from which the power is taken is three-phase, and has a pressure of 10,000 volts at 25 cycles. The potential is reduced by means of a transformer to 220–110 volts. The motor for driving the circulating pump and alternator runs at 220 volts. The alternator generating at 220 volts and 500 cycles is transformed up to 20,000 volts, this high pressure being employed to excite the ozonisers. The process is also in operation in Paris, Dinard, Chantenay, Saint Servain, and other towns in France.

The great advantage in employing ozone for the sterilisation of water supplies which are to be employed for drinking purposes is that no noxious material remains behind in the water. The ozone acts as an oxidising agent, gives up one atom of oxygen in the process, and there remains behind in the water simply oxygen ; that is to say, the water is more thoroughly aerated after the process of ozonisation than before.

I should not be inclined to entirely dispense with filtration, but as the process is so extremely cheap, is so efficient, and so absolutely harmless, it certainly seems that the time has come for sanitary authorities to seriously

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consider the employment of ozone for sterilisation purposes to guard against the outbreak of epidemics.

Other Uses of Ozone.

Ozone is employed for sterilising the air of rooms and buildings. There are various forms of ozonisers employed for this purpose. In one case an ozone tube somewhat similar to the old Siemens tube is fitted on to a fan and rotated with it. The rotation causes air to be drawn through the tube and out again into the air. There is also an apparatus of the Otto type where ozonised air is blown into the room by means of a small electro-motor, which, as it revolves, works a blower and at the same time excites the ozoniser.*

Ozone is also used for maturing wines and in particular spirits. Spirit which would require years for ageing is matured in the space of a few minutes by emulsifying it with ozonised air. It has also been used for sterilising beer-barrels, which have, owing to secondary fermentation, an unpleasant smell, and are known in the trade as "stinkers."

It is also largely employed for bleaching flour and wheat. In this case, however, the apparatus is on a different principle. Ordinary air is passed through the filter and then supplied by a blower to the ozoniser, and thus becomes ozonised. The air is then passed through a spark-box, where a very small proportion of oxides of nitrogen would appear to be produced by the sparks passing in between the sparks in the box. In bleaching the flour the normal amount of air passed through the ozoniser is practically 100 cubic feet per minute. The resulting gas, which is air and ozone mixed with oxides of nitrogen, contains in every 40,000 parts by volume three parts of ozone and one part of oxides of nitrogen. The current is 0·09 ampere and the voltage employed about 10,000. The ozonised air passing at this rate will sterilise and bleach as much as three tons of flour in one hour, which is an extraordinary effect when one considers the small amount of the bleaching agents employed. As showing that sterilisation as well as bleaching takes place, unbleached rye-meal contains 2,400 micro-organisms, and after bleaching 1,600 per grm. Unbleached wheat flour contains 540 organisms and after bleaching 170.

Vanillin is another product which is manufactured by means of the oxidising action of ozone. Eugenol is first converted into izo-eugenol by means of caustic alkali; the alkaline solution of iso-eugenol is then sprayed into a chamber, where it meets a current of ozone, and it is by this means oxidised into vanillin. When crystallised it is ready for the market.

Note.—There has lately been a considerable correspondence in the daily Press in reference to the domestic use of ozone, for sterilisation of water and purification of the air in rooms, &c., it having been maintained that its use in this way is dangerous. Personally, I am not inclined to agree with this dictum. Breathed in large quantities, ozone produces a feeling of nausea, but that quickly goes off, and personally, although I have worked for weeks at a time in a small room the atmosphere of which was saturated with the gas, I have experienced no ill effects. When employed for sterilising water the excess of ozone almost immediately goes off. The personal equation may, however, have something to do with the effect of the gas when breathed in large quantities.

* The Ozonair Company, by means of a fan, draw air through an ozoniser consisting of aluminium gauze separated by a mica dielectric.

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DISCUSSION.

Dr. G. Senter asked whether there was much difficulty in removing the last traces of ozone from the water. He remembered Nernst had once expressed the view that when ozone had stood for some time in contact with water it was difficult, if not impossible, to remove it completely by passing a current of air through the solution. In the portable ozone machines described by the author there did not appear to be any arrangement for the removal of the ozone.

Dr. T. M. Lowry said he had been more impressed with the possibilities of the portable apparatus than with the large sterilisation plants. He thought that a cheaper and simpler way of dealing with town drinking water was to soften it and bring down the bacteria incidentally in the precipitated chalk. This had the advantage of improving the water for steam-raising purposes, and though the process was only in use in chalky districts where the water was so hard as to be a source of annoyance and danger, in domestic hot-water installations he believed it might be extended with very great advantage to waters of slight or moderate hardness.

Dr. V. H. Veley stated that when engaged in attempting to prepare the purest nitric acid possible he had found that the best method for removing the last traces of nitric oxide was to allow the distilled acid to drop through an atmosphere charged with ozone generated in the usual manner. As to the results of the bacteriological examination of water purified by ozone, it was perhaps fortunate for the human race that pathogenic bacteria were, as a rule, the most readily destroyed. Investigations had shown that there were both bacteria and *hypomycetes* (moulds), which were more persistent in their survival, but these were harmless. The speaker thought it was most useful to have on record a careful account of the sterilisation of water by ozone on a manufacturing scale, more especially as in certain processes now before the public they were induced to believe that merely passing an electric current of 30–40 amperes through water brought about ozone sterilisation.

The Chairman: Dr. Perkin has given a very interesting account of the ozonising process, in particular in relation to the purification of polluted water for drinking purposes. I should like to bring before your notice the result of an experiment which I witnessed during a visit last year to Philadelphia. I saw a complete ozone plant for the purification of water, the process being worked by the United Water Improvement Co., at Philadelphia. The plant was erected to treat the foul water obtained from the river Schuylkill, in West Philadelphia, which is described as being nothing but diluted sewage and is estimated to contain as much as 2,500,000 bacteria per square centimetre according to the testings made by the official bacteriologists of the cities of Philadelphia and New York. After a rough straining to remove the coarser particles of suspended matter the water was treated by the ozonising process, and after treatment the bacteria were reduced to an average of about 25, mainly of hay bacillus, which is supposed to have no effect on human organism. The *Bacillus coli*, indicating the organic pollution of water, was claimed to have been completely killed by the ozonising process. The offensive odour was also destroyed and the discoloration of the water was to a great extent removed. The important part of the process of water purification is that it is entirely mechanical and automatic. A pressure of 10,000 volts and 100 cycles was used, and by the operation of re-actant coils and condensers voltaic arcs and sparks are prevented, the current passing as a pencil of blue light from each of some millions of metallic discharge points across a short air-gap to nickel receivers. Atmospheric air is

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drawn across this gap by means of an air-pump, and in so doing is partially converted into ozone. The ozonised air is then forced into a stand-pipe, in which it meets a current of water flowing in the opposite direction. It is claimed that the cost of erection of ozonising plant is not greater than that of the usual method of sand filtration; and it has the undoubted advantage that it only takes a few months to build a large ozonising plant, whereas sand filtration often takes many years to complete. The space occupied is also very small. The plant which I saw in Philadelphia, estimated to be capable of treating for about 30,000 inhabitants, took only 30 by 50 feet of ground against many acres of land which would have been required for sand filters.

The ozonising process has received attention from a very large number of manufacturers, and several processes apart from that so fully described by the author and illustrated with lantern slides are now in use, amongst which may be mentioned also the processes adopted by Messrs. Lahmeyer Co., the Ozonair Syndicate, &c. The size of plant now in use varies, some being capable of treating as much as 5,000,000 gallons per day, like the one erected at Nice. According to the claim made by the inventors the cost of energy for sterilising purposes is very small indeed. It would be interesting to know whether any experiments were carried out in London, and if so, with what results. An important point in favour of the use of ozone for sterilising purposes was the fact mentioned that small complete plants are now available which can easily be transported from place to place, being very useful during military manœuvres or in time of war, &c. The ozone plants can also easily be increased in capacity with the requirements by simply increasing the number of batteries of ozonisers as shown by the author.

It is interesting to notice that this ozonising method is being employed in very small towns, and its future development ought to be carefully watched by all those who take an interest in the purification of water and wish to have it as wholesome as possible for drinking purposes. A simple and compact sterilisation equipment was recently shown by the Lahmeyer Co., at the Municipal Building and Public Health Exhibition held at the Agricultural Hall from May 1st to 12th, and I understand that at the Franco-British Exhibition the Ozonair Syndicate are showing a complete plant in actual operation, indicating the many uses to which ozone could be put. The many recommendations which have been and are constantly being made to boil water before drinking are not as a rule carried out; and although household filters have also been largely recommended, yet these require a great deal of attention and frequent cleansing if they are to answer their purpose satisfactorily. The ozone treatment, it is claimed, kills the dangerous bacteria, and therefore makes the water quite wholesome for drinking purposes. The work of the electrochemist, in improving these processes, is a very useful one, and a great deal may be expected from the extensive use of suitable ozonising apparatus. Time alone will prove their practical value.

Dr. H. Borns would have been glad if Dr. Perkin could have given some information on the French high-tension ozone plants. We had not of late heard anything about the plants of Abraham and Marrier: were they still in existence? It was interesting to learn that the flour process was worked on a large scale by Leetham and Cramp; Alsop, Andrews, and many others had, of course, tried to treat flour with ozone. The figures as to bacteriological tests which Dr. Perkin had quoted went back to 1901 and 1902. A lively controversy had subsequently arisen as to the efficacy of the ozone treatment of potable water, but, so far as the speaker remembered, the result had been favourable to ozone. Paderborn was a town of about 25,000 inhabitants, in

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which Charlemagne had held a Diet in 777. Wiesbaden had itself more than 100,000 inhabitants, he believed, and sheltered at least as many visitors every year. The thermal springs of both these places had been known to the Romans, but the actual Wiesbaden was very modern, also in its claims as to water supply.

Mr. W. Pollard Digby (*communicated*) thought that Dr. Perkin's paper, setting aside the preamble about filtration and its pleas for sterilisation, resolves itself into telling a little more than can be gleaned in *Science Abstracts* upon this subject save for the affirmation "that purification by means of ozone may be said to be electrical, chemical, and mechanical." But the sentence is hardly worthy of a scientist of Dr. Perkin's high standing unless he was jesting. To affirm that purification by ozone is electrical or mechanical has nothing to do with the actual problem of purification. One might as well affirm that in some cases the purification was gaseous and leathery because in certain cases belt-driven centrifugal pumps driven by gas-engines are used in pumping the sewage.

Upon the subject of the purification of impure waters, purification being understood as meaning sterilisation, he had perhaps as close an experience with the problems of water sterilisation as any member of this Society, having worked at this problem under the late Professor Kanthack and under Dr. Rideal in 1897–98; the medium then being used was an electrolytic hypochlorite of soda. These and other experiments were reviewed in a Paper by Mr. H. C. H. Shenton and himself read before the Society of Engineers in 1906.

It would perhaps not be improper in discussing a paper on Ozone to put forward a few figures relating to a product also electrochemical, viz., sodium hypochlorite, which was equally efficacious and far cheaper than ozone.

Dr. Perkin tells us that 13·5 to 27 grammes of ozone are produced per h.p. hour. Taking the higher figure, we thus have a yield of, say, 36 grammes per kw. hour. Now "the water at Paderborn and Wiesbaden requires an average consumption of 1·3 grammes of ozone per cubic metre" (say 230 gallons), so that for a consumption of 1 kw. hour 28 cubic metres of water (of whose composition bacteriologically and chemically nothing is known) can be sterilised. One would probably be wrong in assuming that it was a very bad water, high in organic impurity, akin to the effluent from a sewage settling tank.

Now, it has been established beyond question that 1 grm. of available chlorine in the form of the hypochlorite will sterilise 1·21 cubic metres of settling tank-sewage effluent or 1·5 cubic metres of filtered sewage effluent. In any good electrolyser 1 kw. hour will produce from 150 to 200 grms. of available chlorine. To avoid any imputation of special pleading he would take the lower figure. This, then, gives a sterilisation of 181·5 cubic metres of unfiltered effluent from a settling tank as against a maximum of 28 cubic metres of drinking water of unknown but presumably not greater organic impurity from consumption of 1 kw. hour of electrical energy.

What, then, is to be said of ozone against sodium hypochlorite? Obviously the cost of salt in the latter case. Ignoring the respective capital outlays required, and taking the running costs only, calculating the cost of electrical energy in each case at 1d. per kw. hour and of sodium chloride for the hypochlorite solution at 1d. per 10 lbs. The cost of sterilising Paderborn and Wiesbaden water then becomes 3·57d. per 100 cubic metres.

In 1896–98 his notebooks showed that sodium hypochlorite was being produced at an inclusive charge upon the basis stated of 15d. per kilogramme of

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available chlorine. The cost of sterilising unfiltered sewage-tank effluent was thus 1·24d. per cubic metre.

Dr. F. M. Perkin, in reply to Dr. Senter, said there was no great difficulty in removing the last traces of ozone from the water by simple aeration, and it was possible that the last portion might be removed by coming in contact with organic matter of bacterial nature. Dr. Senter remarked that Nernst considered that when ozone had stood for *some time* in contact with water it was difficult to remove it. In the case in question the ozone was not in contact with the water any length of time, only sufficiently long to destroy bacterial matter.

Dr. Lowry referred to the softening method by precipitating the chalk, which incidentally removes a large amount of the bacteria, but it was doubtful whether bacterial removing action was as efficient as when ozone was employed. He was very much interested in Dr. Veley's remarks, in which he stated that he was able to remove the last traces of nitric oxides by allowing the acid to drop through an atmosphere charged with ozone. He quite agreed with him that the passage of an electric current through water had very little sterilising effect.

Mr. Gaster's experience in America was of interest, and he understood that the Americans are now considering the matter of ozone sterilisation to a very considerable extent, and he was quite in agreement with him that it was very difficult to get householders to filter or boil their water in case of epidemics, and therefore the ozone treatment was much more preferable, especially if the apparatus was fitted to the water supply so as to work automatically.

In reply to Dr. Borns, he was not aware whether the Abraham and Marrier plant was still in existence. The historical facts in reference to Paderborn were very interesting.

In reply to Mr. W. Pollard Digby, he would point out that the ozone processes to which reference had been made were used for the sterilisation of potable water, and he had in no case referred to the sterilisation of sewage effluents. Mr. Digby appears to be wedded to the use of sodium hypochlorite rather than to the use of any other form of sterilisation. Now, sterilisation by means of hypochlorites was an electrochemical process, and sterilisation by means of ozone was also an electrochemical process. For one class of work hypochlorites might be the better and for another class of work ozone; and certainly as far as the sterilisation of potable water was concerned he thought that ozone was very much superior to the use of hypochlorites. When ozone was employed the resulting product was simply oxygen, the extra atom of the oxygen in the ozone being used for oxidising and sterilising purposes. By using hypochlorites sodium chloride was introduced into the water. The quantity, indeed, was small, but at the same time he held that water for potable purposes should have no substance added to it other than oxygen, which is practically the same as giving it a slight excess of aeration. He had often spoken in favour of the employment of hypochlorite for purposes of disinfection, particularly in the case of the very successful Poplar plant, and for treatment of sewage it undoubtedly had shown very good results.

Ozone has not so far been employed to any great extent for the sterilisation of sewage effluent, but provided this were filtered there seems no obvious reason why it should not be used. It would simply be a question of whether hypochlorite or ozone were the cheaper material to use. He was quite willing to admit that Mr. Digby had a large and varied experience in connection with the sterilisation of waters, but his remarks showed that he had had very little experience in sterilisation by means of ozone.

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DETERMINATION OF BOILING POINTS OF VERY SMALL QUANTITIES OF LIQUIDS.

By L. O'DOWD and F. MOLLWO PERKIN.

(*A Paper read before the Faraday Society, Tuesday, May* 12, 1908, Mr. Leon Gaster *in the Chair.*)

The determination of boiling points of very small quantities of liquids by distillation is by no means satisfactory, because in the first place considerable loss in the already small quantity of liquid may take place, and it is difficult to actually arrive at the boiling point owing to the time necessary to heat the thermometer up so that it may show the correct temperature, and the liquid often all distils over before this happens. Various methods have at one time or another been suggested for determining boiling points for very small quantities of liquids, but few of these have been accurate and reliable. Of course it is no use trying to ascertain the boiling point of very small quantities of liquid which is not pure, but it often happens in chemical research that one obtains very small quantities of pure products, and for purposes of identification or even simply to ascertain the boiling point of an unknown substance some reliable method is necessary.

In some textbooks a method is described which, if it gave reliable results, would be very satisfactory. A small glass tube about 6 cm. long and about ¾ cm. in diameter, closed at one end, is fastened by means of a piece of platinum wire against a thermometer, and the thermometer and tube are fixed by means of a clamp into a beaker containing sulphuric acid or other liquid of high boiling point. The beaker is fitted with a stirrer in the ordinary way. The determination of the boiling point is made by placing 1 cm. of the liquid into this little test-tube; then a capillary tube, which is sealed together about 1 c.c. from its end, is also placed into it so that the liquid reaches about up to the sealed part of the capillary. The directions for taking the boiling points are as follows :—

The liquid in the beaker is heated by means of a burner, and in order to insure the steady rise of temperature it is agitated by means of the stirrer. When the liquid in the test-tube has nearly reached its boiling point bubbles of air commence to rise up through the liquid from the end of the capillary. The burner is now removed from below the beaker and the liquid thoroughly agitated so that the temperature may be uniform. It is then again replaced for a short time and again removed, these operations being repeated so that the rise of the temperature may be easily noted from degree to degree. As the boiling point is neared bubbles of air rise more rapidly, until when the liquid is just boiling they are given off in a continuous chain. At this point the thermometer is read, and by repeating the operation two or three times, each time putting a fresh capillary in, it is said to be possible to obtain close results. We very carefully tried this method but found it to be anything but accurate.

With moderately low boiling substances the temperature might be ascertained within two or three degrees. With very low boiling substances it is

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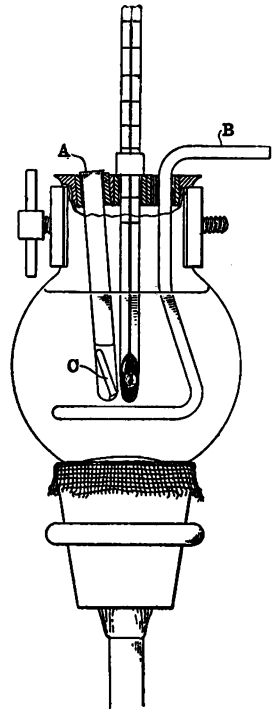
quite inaccurate, and with high boiling substances it was also not to be depended upon. We then tried various methods of modifying this process in order to see whether it might be possible to make it accurate. For example, a piece of platinum wire was fused through the end to the small test-tube, and an improvement was undoubtedly obtained, but even yet the results were by no means accurate. Finally, we devised the following process, which gives results leaving very little to be desired. The apparatus is depicted in the diagram. A flask *A* which holds about



100–110 c.c. of fluid is placed upon a wire gauze fastened over an inverted cone, such as is used to prevent Bunsen burners from flickering. The object of using this kind of chimney is that the heat may be evenly distributed upon the bottom of the flask. The flask has a very wide neck, about 4 cm. in diameter, which is fitted with a cork having three holes bored in it. Through the central hole a thermometer is passed, and through *B* a small thin-walled test-tube, about 7–8 cm. long, and having a diameter of ¾ cm. This tube, however, is not passed directly through the cork but passed through a piece of glass tubing which is fitted into a cork so that it may be inserted and withdrawn without any difficulty. And, furthermore, if it happens to be moist with sulphuric acid, should this be the heated liquid employed, the cork will not be charred. In order to prevent the tube from slipping through into the flask the top of it is slightly widened out, so as to act as a collar. The thermometer also passes through a similar tube, and to prevent it dropping down too low a piece of rubber tubing *C* is placed round it to act as a support. The stirrer *D* of glass rod fits loosely through another tube, so that the air, as it expands upon heating, shall not set up a pressure.

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About ½ c.c. of liquid, the boiling point of which is to be determined, is placed into the tube, and then a capillary tube, sealed at one end, and about 1–1½ cm. long, is dropped into the liquid in such a way that the open end is to the bottom. The determination is then carried out as follows :—

The temperature is raised by means of a Bunsen burner, the liquid being gently stirred in the meanwhile. The temperature is raised fairly quickly at first until a continuous stream of bubbles is given off from the bottom of the capillary tube. The source of heat is then removed and the temperature allowed to drop, the heating liquid being thoroughly stirred while it cools. As the temperature drops the bubbles begin to be given off less rapidly, and finally stop altogether. At the moment the bubbles cease to be given off—that is, when the pressure of the vapour within the tube is equal to the atmospheric pressure—the thermometer is read off and this is the boiling point of the liquid. A second determination can be made by at once again rapidly rising the temperature before the liquid is sucked back into the capillary tube. The stream of bubbles is again obtained, and on cooling down a second reading may be taken as before. It is found that by proceeding in this manner, and being careful to stir, absolutely accurate results may be obtained. If the liquid is not stirred the results are by no means accurate. This is, we think, due to the condensed vapour which has risen up in the tube *B*, which, being cooler than the heating bath, runs down to the liquid and stops it boiling. This, however, does not affect the thermometer sufficiently rapidly to drop the mercury, consequently the liquid ceases boiling inside the tube *B* and too high a boiling point is registered by the thermometer.

We append a table of boiling points obtained by this apparatus.

Column 1 gives the actual boiling point, those marked in asterisk having been obtained by previous distillation with the same thermometer, the others being the known boiling points of the substances taken from the literature.

Column 2 gives the boiling point obtained with this apparatus when stirrer was used.

Column 3 gives the results when no stirrer was employed.

	Mean Experimental Boiling Point.		
	Actual Boiling Point.	With Stirrer.	Without.
Ether	*35–36°	35·75°	—
Acetone	*56·5–57°	56·8°	—
Hexane	*67°	67·0°	—
Distilled Water	100°	—	100·0°
Ethyl propionate... ...	*98·0°	98·2°	99·5°
Anisole	155°	—	154·5°
Aniline	184·0°	—	184·0°
Nitrobenzene	*206°	206·0°	209·0°
Safrol	*231–231·5°	231·2°	234·0°

It is obvious that, with efficient stirring during cooling, the closeness with which the temperature of the inner liquid keeps to that of the outer depends on the rate of cooling, and this in turn depends upon the volume of the outer liquid. If, therefore, great accuracy is required, it is only necessary to employ a standard thermometer, a large flask to contain the heating liquid, and, perhaps, a mechanical stirrer. Now, as the rate of cooling at any time depends upon the difference of temperature between the liquid and the air

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the same amount of accuracy can be obtained for low temperatures by using a much smaller flask than would be necessary for high temperatures, because the cooling is slower when the temperature approaches that of the atmosphere. It is also an all-important feature that the small test-tube should dip well into the heating liquid to ensure thorough heating of the condensed liquid within the tube, because this runs back down the sides and would otherwise stop the boiling. And, finally, the thermometer should be read when the inner liquid ceases to give off vapour—that is, when the last bubble stops increasing in size. Under these circumstances, all errors due to thickness of glass, &c., may be neglected. After being in use for some little time the sulphuric acid becomes dark in colour. This can be prevented and the acid again be rendered colourless by the addition of a few small crystals of potassium nitrate, which are easily dropped in by removing the small tube.

DISCUSSION.

Dr. Senter asked if it was quite certain that the outside liquid had the same temperature as that in the small tube containing the capillary when the reading was made.

Dr. Perkin, in reply, said that the boiling point of the liquid in the small tube was obviously the same as the temperature of the outer liquid, because in the table given the boiling points marked with an asterisk were first obtained by distillation, using the same thermometer, and it will be noticed that the results obtained by the other method are almost identical.

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ON THE UTILISATION OF THE ATMOSPHERIC NITROGEN IN THE PRODUCTION OF CALCIUM CYANAMIDE, AND ITS USE IN AGRICULTURE AND CHEMISTRY.

By Dr. ALBERT R. FRANK.

(*A Paper read before the Faraday Society on Tuesday, June* 9, 1908, Dr. F. Mollwo Perkin *in the Chair.*)

When Liebig, about the middle of last century, laid down the scientific basis of the natural laws of agriculture and the cultivation of plants, he showed that the essential condition for ensuring the soil against loss of plant-food, and thereby enabling it to maintain its fertility, was the supply of such *mineral* foods as the plants require for their growth. These mineral foods are continually being withdrawn from the soil, where they are by no means over-abundant in available form, by the crops. Among such foods Liebig placed phosphates and salts of potassium in the front rank, and thus founded his theory of *mineral manure.* As regards bodies like oxygen, hydrogen, carbon, and nitrogen, which are used for building up the intrinsic organic plant substances, Liebig maintained, in opposition to the supporters of the vegetable theory, which was believed in up till then, that the requirements of vegetation were continually and adequately supplied by the atmosphere, and that the effect of the nitrogen contained in certain bodies widely known in practice as efficacious manures, such as bone ash and guano, was of less importance than that of the other inorganic plant foods. Technical chemists adopted Liebig's suggestion with enthusiasm and success. After the discovery of the rich mineral phosphate deposits, the conversion of these into the higher phosphates by treatment with sulphuric acid was utilised with much success. The author's father, Professor A. Frank, of Charlottenburg, succeeded, after the Stassfurt deposits were discovered, in placing at the disposal of agriculturists, the world over, an inexhaustible supply of the much needed potassium salts. As a result of the successes achieved in agriculture by Liebig's *mineral* theory, observant investigators, and amongst the first of these Liebig himself, could not in the long run ignore the fact that, by the addition of bodies containing nitrogen to the mineral manures, an essential requirement of plant life was met, and, at the same time, an improvement in the financial condition of the manure trade must ensue. In consequence an immediate demand for manures containing nitrogen, most of them of organic origin—*e.g.*, bones, blood, offal, and fish guano—arose. These, however, only partially supplied requirements, while at the same time the Peruvian deposits of animal guanos were being very rapidly depleted by an ever increasing demand. It became necessary, therefore, to turn to those inorganic compounds of nitrogen which had definitely been proved by scientific research to be suitable for plant food. Of these the two most important were the salts of ammonia, especially ammonium sulphate, the manufacture of which on a large scale from the gas liquors was first carried out in England in the early sixties, and the nitrates, of which an extensive deposit, in the form of sodium nitrate, was discovered on the rainless plateaus of Peru and Chili as early as 1830. Their application to agriculture, however, dates from 1860. Since ammonium salts

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have up till now only been profitably obtained as a by-product in the manufacture of coal, gas, and coke, their production, in spite of the great increase from 10,000 tons in 1860 to about 600,000 tons last year (of which England uses up some 316,000 tons), is limited and dependent on other factors than agricultural demand.

OUTPUT OF AMMONIUM SULPHATE IN ENGLAND.

Year.	Total Production.	Average Price Per Ton.	Total Home Consumption.	Used in Agriculture.
	Tons.	£ s. d.	Tons.	
1898	196,500	9 2 7½	65,000	This may be anything between 90 to 75 per cent. of the total home consumption, the balance being absorbed in arts and manufacture.
1899	208,000	11 5 9¾	58,500	
1900	210,000	11 2 0	65,000	
1901	228,500	10 11 4	68,297	
1902	229,000	11 16 3	68,700	
1903	234,000	12 9 3	70,200	
1904	245,000	12 3 8	71,200	
1905	268,500	12 10 9	75,400	
1906	289,000	12 0 9	78,000	
1907	316,000	11 15 3	87,500	

OUTPUT OF AMMONIUM SULPHATE IN GERMANY.

Year.	Total.	From Coke.	From Gas Works.
	Tons.	Tons.	Tons.
1897	84,000	70,000	14,000
1898	98,000	84,000	14,000
1899	100,000	84,500	15,500
1900	106,500	88,500	18,000
1901	133,000	113,000	20,000
1902	140,000	117,000	23,000
1903	146,000	120,000	26,000
1904	182,000	152,000	30,000
1905	203,000	168,000	35,000
1906	235,000	197,000	38,000

It was these circumstances which placed sodium nitrate in the front rank of nitrogenous manures, and which caused the world's demand for these substances to rise from 935 tons in 1830 to about 1,740,000 in 1907 (see Fig. 1).

Of this amount Europe absorbs 1,400,000 tons and the U.S.A. about 340,000 tons, 20–25 per cent. of this being employed in the manufacture of chemicals and explosives, while the rest is used for agricultural purposes. Germany, which on account of the uncertain climate of its northern provinces, and because of its extensive beet sugar industries specially needs manures, is the largest consumer, importing over 500,000 tons yearly, about 400,000 of which are utilised in agriculture. The guano deposits which at first were considered inexhaustible have now practically come to an end, and the same remark applies to the strictly limited nitrate deposits in the rainless region of Western South America. Agriculturists and political economists naturally regard with considerable anxiety the approaching disappearance of the deposits, while the demand for nitrates is steadily increasing year by year. Whether the date of exhaustion will be twenty or forty years hence is, on account of the vast

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importance of the question, of little consequence, seeing that even during the last few years the price of sodium nitrate has risen 35 to 40 per cent. (in Germany), an increase due less to speculators than to higher working expenses and growing difficulty of production. It is also manifest that the chemical industries can afford to pay for the nitrate—which they consume in the production of nitrogenous compounds, nitric acid, and explosives—higher prices than the agriculturist is able to give. The price of sodium nitrate reveals, in addition, the state of the market for other nitrogenous manures. Ammonia and ammonium salts have likewise shown a marked advance, and agriculturists who have urgent need of these manures, not only for producing their present average crops, but also for securing the increased output made necessary by the growth of population, an urgent necessity pointed out some years ago by Sir William Crookes, were threatened with a serious nitrogen famine.

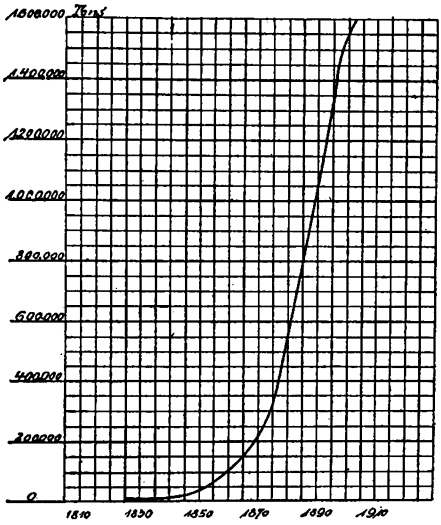

FIG. 1.—SALTPETRE PRODUCTION IN CHILI.

It is well known to all that the atmosphere surrounding our earth contains a diffused and practically inexhaustible supply of nitrogen, totalling about 4,041,200,000,000,000 tons. This works out at 31,000 tons of nitrogen over each acre of the surface of the globe, or the still air over every nine acres contains about 280,000 tons—*i.e.*, the same amount which is contained in the 1,740,000 tons of Chile saltpetre exported from that country in 1907. We know, further, that uncultivated plants, partly through certain organs which exist in them, as well as in leguminous plants, and partly by the aid of bacteria inhabiting the soil, are able to absorb the nitrogen they require from the air diffused through the soil. Furthermore in 1775 Priestley showed that atmospheric nitrogen under the influence of the electric spark combined with atmospheric oxygen to form nitric acid, the latter being conveyed by moisture to the soil and then to the plants. But all this accumulated experimental knowledge, important though its results undoubtedly were, did not afford any clue to the possibility of producing nitrogen compounds in considerable masses, nor was it freely at the disposal of agriculturist or chemist. The method devised by Fownes and Young last century, and experimentally applied by Bunsen and Playfair, showed that by passing atmospheric nitrogen over carbon and the alkalies or alkaline earths, the carbon compound

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cyanogen could be formed from which by further treatment ammonia could be obtained. This method, in spite of its extensive application and the many improvements which Marguerite and Sourdeval and later Ludwig Mond introduced in its technical details, produced no practical result, on account of the difficulty of attaining the requisite temperature. It was further complicated by the fact that the construction and maintenance of the apparatus, owing to the materials used in the furnaces, gave rise to what were then insuperable difficulties. The first successful advance was made through the discovery and application of the dynamo, which rendered it possible for electricity to be supplied in considerable quantities. By this means a hitherto unattainable temperature could be produced in quite a restricted space. Up to this time, now some few years ago, the necessary energy had to be obtained, except in so far as it was produced by reaction from the molecular energy of the elements, by means of the chemical process of "combustion." With the application of the dynamo and the invention of the electric furnace by Siemens, this process was greatly modified, as by means of electric energy thus applied heat could be produced by means of the electric arc or of an electrical resistance, and could be brought to bear directly on to the chemically reacting mixture.

With these improved means at their disposal, investigators endeavoured once more to find a solution, as already stated, of the all-important question of the fixation of nitrogen.

Subsequent to 1894, when Thomas L. Willson and Moissan carried on the manufacture of carbide on a large scale in the electric furnace, the author's father, Prof. A. Frank, in a Paper[1] published in February, 1895, opposed Moissan's views as regards the possible use of this carbide combined with atmospheric nitrogen, for the preparation of cyanides and amides. Tests carried out in conjunction with Dr. N. Caro on this point established the truth of his hypotheses and further led to the invention of a method for the preparation of cyanides, cyanamides, ammonia, and other nitrogen compounds. It is on the technical and industrial manufacture of these and their value that the author has this evening to speak to you.

The other way of fixing nitrogen, on which much successful work has been accomplished, by oxidising it and turning it into nitric and nitrous acid by means of the electric spark, was soon established on practical lines, firstly with unsatisfactory technical results at Niagara Falls by Bradely & Lovejoy, and then by the magnificent discovery of Birkeland & Eyde, as well as by the improvements which are now being perfected due to Schönherr and the Badische Anilin and Soda Fabrik. Prof. Birkeland made some highly interesting remarks on the oxidation of atmospheric nitrogen in this room in July, 1906, which you will all remember. In amplification of these the author may add that the production of calcium nitrate by the Birkeland-Eyde process seems to be developing exceedingly well in Norway, and that the factory mentioned by Prof. Birkeland is actually established at Notodden and is producing this substance. It should, however, be noticed that this industry has not made much progress in any other land save Norway, but it should not be forgotten that it is only in this Northern clime that electrical energy can be as cheaply obtained on account of its unrivalled resources of water power. It would therefore seem probable that Norwegian saltpetre is destined to remain the only direct competitor of the Chilian variety.

As will be seen later on in my Paper, the two methods of nitrogen fixation

[1] *Verhandlungen des Vereins zur Beförderung des Gewerbfleisses*, 1895, No. 2, February: "Über Gewinnung von Acetylen und dessen Verwendung zur Herstellung von Alkohol," &c. By Dr. Adolph Frank Charlottenburg.

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differ greatly as regards their chemistry. Physically they are similar; for, properly speaking, they are not electrical, but should be considered purely thermal processes. They do, however, differ in that the fixation of nitrogen by carbide is an exothermic process, in which heat is given out, while the combination of oxygen and nitrogen is endothermic—*i.e.*, it absorbs a large amount of heat, and for the fixation of an equal quantity of nitrogen requires at least three times the energy that the former process calls for.

The researches instituted, as mentioned above, by Frank & Caro in 1895 were first carried out on calcium carbide mixed with sodium carbonate. But as the yield of cyanide obtained in this way proved unsatisfactory, they soon substituted carbide of barium therefor, a substance which at that time could be more easily obtained, and this they found absorbed nitrogen isolated from the air with great avidity at a temperature of between 700° and 800° C. Frank and Caro were then contemplating the transformation of barium cyanide by treatment with carbonate of sodium or potassium into cyanide of potassium, which at that time commanded a very high price, with a considerably increasing demand. The first experimental plant was constructed with the object of perfecting as far as possible the process for obtaining cyanide of potassium and yellow prussiate. They soon found that the nitrogen absorbed by barium carbide was not merely in the form of cyanide ($Ba(CN)_2$), but that it was also present in the form of a more complex compound. The latter was found, on examination, to be cyanamide of barium $BaCN_2$, from which they inferred that the reaction had taken place according to the following equation—

$$BaC_2 + 2N = BaCN_2 + C.$$

Thus it appeared that in the reaction of carbide on nitrogen half of the carbon contained in the carbide had been set free. The proportion of cyanide and cyanamide of barium in the reacting mass was on an average as two to three, the product containing 30 per cent. of barium cyanide and 45 per cent. of barium cyanamide, the remainder consisting of barium oxide and carbon.

The transformation of the barium cyanamide into barium cyanide could be easily brought about by melting the mass containing both cyanamide and cyanide, with a flux such as potash or soda according to the following equation—

$$Ba(CN)_2 + BaCN_2 + C + 2K_2CO_3 = 4KCN + 2BaCO_3.$$

The great progress which had meanwhile been made in manufacturing carbide of calcium on an industrial scale gave rise to a renewed attempt to try again the method of treating carbide of calcium with nitrogen, which had been previously abandoned owing to the difficulties which it offered at first starting.

It was then discovered that the small yield of cyanide obtained in using carbide of calcium without an additional flux could be further reduced, and that no cyanide need be formed at all, but that the reaction would proceed in accordance with the following equation—

$$CaC_2 + 2N = CaCN_2 + C,$$

and result in the formation of cyanamide of calcium alone, whilst, as has been seen, in using carbide of barium the corresponding cyanide was also formed.

About this time the patentees, Messrs. Frank and Caro, together with the well-known electrical firm Siemens and Halske, and the Deutsche

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Bank of Berlin, founded the Cyanid Gesellschaft of Berlin, for the further development of the process. The primary object of the new Company in taking up these inventions was to turn cyanamide of calcium into cyanide of potassium, for which there was an extensive and increasing demand for the purposes of gold extraction in South Africa and the United States. It is common knowledge that this object was successfully accomplished.

The low atomic weight of calcium carbide compared with barium carbide, owing to which 64 parts in weight of calcium carbide sufficed to bind about 28 parts of nitrogen, seemed to point to the conclusion that by using calcium carbide it might prove feasible to produce those nitrogenous compounds also in which the nitrogen would only command a low price, such as fertilisers, &c. Further research in this direction was starting with calcium cyanamide as the raw material for producing ammonia, especially when it turned out that the total nitrogen contents of the calcium cyanamide could by treatment with hot water be turned into ammonia without any difficulty or loss. The process is effected according to the following equation—

$$CaCN_2 + 3H_2O = CaCO_3 + 2(NH_3).$$

In spite of the fact that this reaction requires an excess of water and a high temperature, and that acknowledged authorities on agricultural subjects passed unfavourable opinions in view of the presence of the poisonous cyanide group in the product, in consequence of á proposal made by me, an attempt was made to utilise crude calcium cyanamide directly as a fertiliser, burying it in the ground like any other manure. These experiments were first carried out in pots only. The results were satisfactory enough to indicate that the doubts entertained as to the applicability of the product as a fertiliser were groundless. Thereupon field experiments were arranged on an adequate scale at a large number of agricultural experimental stations, in most countries possessing agricultural interests, and in connection with almost every class of agricultural produce, and these have been continued for the last six years without intermission.[1]

As has been the case with many other artificial manures, a great outcry was, and still is, made warning farmers against the use of calcium cyanamide, popularly known as nitrolim, or at least advising that it should be employed with the utmost caution. This outcry originated in the fact that not only farmers but even agriculturists are saturated with intense conservatism, and that initial failures did here and there occur when first using calcium cyanamide. It is, however, certain that manufacturers must in the first instance determine the most suitable form for every new manure, as a string of well-known instances in the case of other manures abundantly proves. Fifty years ago, when the author's father proposed the use of the potassium salts in the Stassfurt deposits, the chlorine compounds of potassium were not only considered as of doubtful value, but even as harmful, while to-day three million tons per annum are used in agriculture all the world over. In the same way there was a time when the use of Chili saltpetre was directly forbidden by the contracts of beet sugar manufacturers, while to-day it is considered absolutely infallible by *all* agriculturists, and in certain processes quite indispensable. The storm raised against calcium cyanamide has been lulled in the same way, and recently Professor Wagner of Darmstadt, one of the greatest authorities on agricultural chemistry, summed up his exhaustive researches

[1] Experiments in the United Kingdom with the new manure have been made at Rothampsted, the Cambridge University Farm, the West of Scotland Agricultural College, Harper Adams Agricultural College, the Highland Agricultural Society, the Dauntsey Agricultural School, and many other agricultural stations.

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on the nitrogenous manuring of plants with Chili saltpetre, salts of ammonia, and calcium cyanamide as follows: "The prospects for an advantageous use of calcium cyanamide are very bright, especially as regards its use for winter fruits. Calcium cyanamide can only be harmful in agricultural practice when it is submitted to abnormal decomposition through *unfavourable* circumstances. Such conditions are especially present in the cultivation of poor lands, such as high moorland and sandy soils which are inclined to be acid, and though rich in vegetable properties are poor in lime. It is, however, well known that this *soil behaves in an abnormal manner to other nitrogenous manures.* In order to prevent the unsuitable conditions of acid soil previous liming is necessary."

It was, besides, only natural that the manufacturers who were not in a position to turn out manure in bulk complying with all these demands should not have been very favourable. To-day, however, things are very different. A product is actually manufactured containing 20 per cent. and upwards of nitrogen—that is, considerably more than did the earlier products—which recently has further been submitted to a successful dust-removing process, is packed in air-tight sacks, and its efficacy appreciably increased thereby; there can be no longer any doubt that calcium cyanamide is in a position to compete industrially with any other nitrogenous manure. In this connection the question of price is of the highest importance. Now, as the cyanamide industry has been perfected in the course of the last few years, it must be considered to form, on the basis of the percentage of available nitrogen, the cheapest, and therefore for agriculturists the most economical, manure of the present time. When the first consignments of calcium cyanamide were placed on the market the question of packing and storing was not fully understood. The result was that the product, containing a large amount of free lime, under the influence of atmospheric moisture was naturally converted into calcium hydrate. This caused such a large increase in the volume of the material that the jute sacks containing it burst. The theoretical proportion of nitrogen showed a decrease which was not ascribed, as it should have been, to the increase in total weight but was thought to be due to the fact that nitrolim lost nitrogen in some form or other when stored. Scientific research has shown conclusively, however, that calcium cyanamide may be kept stable for years without losing its nitrogen. The technical authorities have also taken notice of this fault, as mentioned above, and calcium cyanamide is now supplied by the manufacturers practically free from the influence of atmospheric moisture and packed in double paper and jute sacks.

It has a further merit, which is of great importance in agricultural operations where elaborate appliances are wanting: calcium cyanamide can be mixed with most widely different manures without loss. For instance, mixed manures of cyanamide and potassium salts, basic slag, &c., may be mentioned which have been found eminently successful in practice. Some difficulty is met in mixing cyanamide with super-phosphate, as the free phosphoric acid combines with the free lime of the cyanamide, and is changed from the water soluble to the citric soluble form. To a certain extent this is not preventable, but the interesting and exhaustive work of Professor Hall, the well-known agricultural chemist and director of the Rothamstead agricultural farm, on this subject has proved that by observing certain conditions the mixing of super-phosphate with cyanamide can be easily accomplished, and is both successful and economical.

What makes cyanamide especially valuable as a manure is its after-effects. It is generally decomposed by the chemical and bacteriological constituents of the soil into ammonia, which becomes fixed by the vegetable mould, and

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is not, as is Chili saltpetre, liable to be washed into the drains and so practically lost. For this reason cyanamide which has not been used during the *first* harvest is always available for the *second*. Researches on this subject show that the after-effects of cyanamide can be very considerable according to circumstances, a property possessed by no other nitrogenous manure. As regards the economy effected by cyanamide manuring the author will shortly describe the great number of tests which have been carried out for more than six years at agricultural research stations and by users in all parts of the world, and render the operation of cyanamide apparent by the help of photographs (see Appendix No. I.).

As regards the part which cyanamide or nitrolim plays in the soil various theories have been propounded. It appears that when brought in contact with the ground calcium cyanamide is first decomposed through the action of the moisture and of the carbonic acid in the soil into free cyanamide and carbonate of lime according to the formula—

$$CaCN_2 - H_2O - CO_2\ H_2CN_2 - CaCO_3.$$

The free cyanamide will then, by absorbing water, probably be further decomposed into urea—

$$H_2CN_2 + H_2O = CO\begin{matrix}NH_2\\NH_2\end{matrix}.$$

The final product of this decomposition has been found to be ammonia, but later nitrate is produced through the nitrification of the ammonia. Special experiments have demonstrated that the process of transformation of calcium cyanamide or nitrolim is assisted by a host of microbes which are to be found in almost all cultivated soil. On this point very important and interesting investigation has been carried out quite recently by Dr. Löhnis and Sabaschnikoff[1] of Leipzig, and Dr. R. Perotti of Rome.[2]

It is, however, not only to the production of fertilisers that the scope of the new calcium cyanamide industry has been limited, for it has been also successfully extended to the production from nitrolim of a number of chemical substances to a great extent by utilising derivative forms of reaction long known to science. I am able to show you here some small samples of several of these derived products, all obtained from cyanamide of calcium. Although calcium cyanamide does not display the typical character of the cyanamides, it can, by melting with fluxes, be turned into calcium cyanide, which product can then be treated by well-known methods to yellow prussiate or cyanide of potassium or sodium. The molten mass obtained by melting nitrolim with a flux contains approximately an amount of cyanide corresponding to 25 per cent. KCN., the cost of the said molten mixture, to which we have given the name of "surrogate," being much less than that of an equivalent amount of pure cyanide of potassium, and the material having been shown by the investigations of English experts to be of equal efficiency with pure cyanide of potassium for the extraction of gold and silver. It appears particularly suited to the requirements of the countries where gold and silver are mined, as it can be produced without difficulty at the mine itself where it is to be used.

The production of ammonia and ammoniacal salts from nitrolim, to which I have made reference previously, has also been further worked out and

[1] *Untersuchungen über Kalkstickstoff und Stickstoffkalk*, von Dr. Alexis Sabaschnikoff. Berlin: 1908, Verlag von Paul Pavey.

[2] Dottore Renato Perotti, *Su i bacteri della diciandiamide*. Roma Typographia Enriev Voghera, 1908.

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perfected on an industrial scale. You will readily understand that the ammonia obtained by heating $CaCN_2$ with water is very pure and free of empyrheuma. It is therefore particularly suitable for the production of pure ammoniacal salts as well as liquid ammonia (see Fig. 2).

Further, the author would point out that a number of complex organic nitrogenous compounds have been derived from calcium cyanamide, and are already being produced on a manufacturing scale. Out of the great number of these I will only mention dicyandiamide $(CNNH_2)_2$, for which there is an increasing demand in Germany for the manufacture of organic dyes, besides which there are urea $CONH_2$ and sulphourea $CSNH_2NH_2$.

The author would also mention that one of the German companies is producing from nitrolim the salts of guanidine, such as carbonate and nitrate of guanidine, nitro-guanidine, and other salts, all of which should now gradually come into use on an increasing scale in the industries of organic chemistry, as the cost of production will be considerably lower when starting from calcium cyanamide than by the methods of manufacture hitherto employed. Recently attention has been paid to the use of nitrate

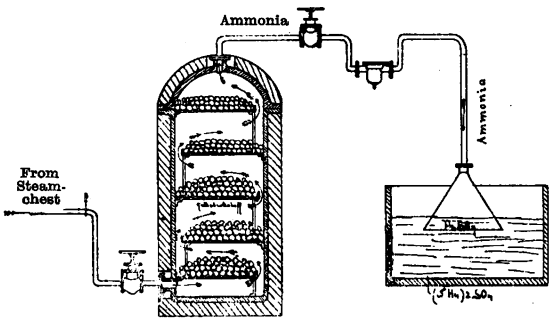

FIG. 2.—DIAGRAM OF A PLANT FOR AMMONIA PRODUCTION FROM LIME NITROGEN.

of guanidine, nitro-guanidine, and dicyandiamide as a "deterrent" for reducing the temperature of combustion with explosives and gunpowder. In consequence of the high contents of inert nitrogen in dicyandiamide (66·6 per cent.) it evolves a strong pressure when burnt in a gun, and in contradistinction to the other constituents of the explosive which contain more carbon and hydrogen, its decomposition produces but little heat. This peculiarity is of great importance in powder used with ordnance, such as cordite and filite, which, because of the high temperature of combustion, rapidly destroy the rifling of the barrels. With many powder mixtures the cooling action of dicyandiamide is shown by the disappearance of the flash at the muzzle, so that on discharge both powder smoke and powder flash are done away with.

The composition of the crude cyanamide of calcium made it appear likely that it would lend itself quite as well as yellow prussiate and potassium cyanide for use in case-hardening and tempering of iron and steel. Tests carried out to this end have confirmed this impression. It has been shown that by adding certain fluxes to the crude cyanamide of calcium a very high hardening effect can be produced. This new hardening mixture, under the name "ferrodur," has been introduced on the market in Germany, England, and other countries, and its property of producing an extraordinary depth of the hardened surface without the material being at all deteriorated has already secured it a great number of friends.

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If I may ask your indulgence for a few more minutes, I would like to give you a short description of the method by which the nitrolim is being produced in some of the factories, and to say also a few words on its position in the markets of the world. The carbide coming from the electric furnaces is ground, charged into retorts made of fire-proof material which are mounted in a furnace similar to gas-house furnaces (see Fig. 3). The nitrogen is then passed over the carbide at a temperature of from 800° to 1,000° C. The carbide used is of the same quality and percentage as that employed for lighting purposes, and the nitrogen consumed is obtained by fractional distillation of liquefied air by the Linde system, or the so-called "copper" process in which air has passed through heated copper particles. The copper takes up the oxygen and the free nitrogen passes to the furnaces. The resulting copper oxide is reduced in the same apparatus by treatment with reducing gases or vapours, and the copper which is recovered is then ready for a new cycle. In the Linde process the oxygen remaining after separation of the nitrogen may be utilised for any purposes. As soon as the carbide in the retorts is saturated with nitrogen, a fact which will be made apparent by the controlling gas-meter coming to a standstill, the calcium cyanamide is extracted from the retorts in the form of a hard cake and cooled while the air is excluded. It is then ground into a fine powder and is ready for use.

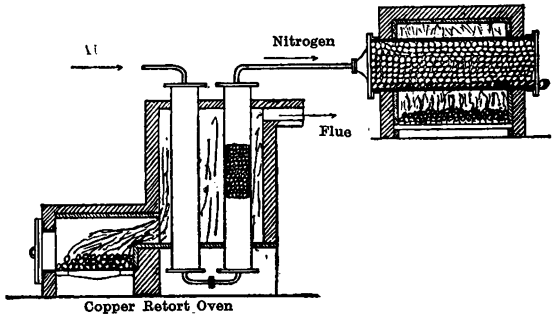

FIG. 3.—DIAGRAM OF A LIME NITROGEN PLANT.

During the last year a new electric furnace has been developed for treating carbide with nitrogen, and is being universally adopted by all the new cyanamide factories in preference to the older retorts. This process is cheaper to install and to operate where the cost of power is low compared with that of the retort furnaces just described; and notwithstanding that the average life of the retorts has been greatly prolonged, the new electric furnace is cheaper to maintain, possessing practically an unlimited life.

Crude nitrolim contains about 57-63 per cent. of the pure cyanamide of calcium, so that its total contents in nitrogen will amount to roundly 20–22 per cent., the same as sulphate of ammonia. The material contains besides this about 20 per cent. of calcium oxide, 7–8 per cent. of silicious acid, iron oxide and alumina, and 14 per cent. of carbon, which imparts to the product its characteristic slate-black colour.

Most carbide works obtain at the present time a yield of two tons of carbide per kw. year, and two tons of carbide will combine with practically 500 kilograms of nitrogen in the form of nitrolim; a power of two kw. or $2\frac{2}{3}$ horse-power is required per year for fixing one ton of nitrogen by the Frank-Caro process. In addition thereto, about $\frac{1}{3}$ horse-power is required for grinding and all other operations. If, therefore, it were pro-

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posed to substitute nitrolim for the nitrate of soda at present consumed in the world, it would require plants disposing of no less than 800,000 horse-power to do so.

It goes without saying that before the process of making nitrolim could be developed on an industrial scale, its value as a fertiliser had first to be ascertained. And as it naturally took a number of years to complete the exhaustive agricultural researches instituted for this purpose sufficiently to make them conclusive, it will not surprise you, gentlemen, that it was only about three years ago that the question of putting up industrial works was attacked.

About that time the Cyanid-Gesellschaft, in conjunction with two important Italian companies chiefly interested in the manufacture of calcium carbide, promoted, under the management of Cav-Morani, the founder of the Italian Carbide Industry, the Societa Generale per la Cianamide in Rome.

The first plant on a large industrial scale was started about two and a half years ago at Piano d'Orta in Central Italy (Figs. 4 to 8), near to the Adriatic Sea, for a yearly production of 4,000 tons of lime nitrogen, and is just now being enlarged to a capacity of 10,000 tons. In addition to this, the Societa Generale is also about to appropriate a large water-power it owns in Italy for the erection of other works. One is ready to start in Terni in connection with the large carbide factories there, and another factory is in course of erection in San Marcel in the Val d'Aosta.

There are at present in Austria-Hungary important cyanamide works in course of erection, all promoted by the Societa Generale of Rome. In Sebenico, in Dalmatia, at the carbide works one is being built for an initial yearly production of 4,000 tons. At Fiume, in Istria, works are also in construction for a similar output.

At the present time a water-power installation of at least 50,000 horse-power is being erected at Almissa, also in Dalmatia, for the manufacture of this new artificial manure. The market for the products of these works will be the Balkans, Asia Minor, and Egypt, where, owing to the practice of irrigation, nitrolim will be of special value to agriculture.

In France, the Société Francaise des Produits Azotés installed works a few months ago at Nôtre Dame de Briançon (Haute Savoie), for the manufacture of cyanamide, with an output of about 4,000 tons per annum. In the Rhone Valley in Switzerland the Société Suisse des Produits Azotés has just opened equally important works. In Germany, the works at Westeregeln and Brühl on the Rhine are manufacturing 10,000 tons of nitrolim annually. It is interesting to mention that the works at Brühl for the preparation of carbide do not employ water-power, but produce the power required in the works themselves, using cheap coal in large quantities for this purpose. Another installation is that of the Brandenburgischer Carbidwerke for the preparation of nitrolim with an output of 2,500 tons per annum, near Bromberg, in North Germany, which is also completed, while the large works of the Cyanid Gesellschaft for an output of over 15,000 tons of nitrolim at Alz-Fluss, in Bavaria, are at present in construction. In the United States of North America the American Cyanamide Company has taken up the manufacture of nitrolim, and are constructing on the Canadian side of the Niagara Falls works of a present capacity of from 5,000 to 6,000 tons per annum, to be enlarged later to an output of 40,000 tons.

It is quite natural that English enterprise should have given this new artificial fertiliser considerable attention. The North-Western Cyanamide Co., Ltd., with a capital of £120,000, was incorporated in the middle of 1906 to acquire from the Societa Generale and work licences for the manufacture

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and sale of cyanamide in a vast territory comprising the United Kingdom, the Colonies, Protectorates and Dependencies (excepting Canada and Egypt), and a large portion of the North-West of Europe, viz., Norway, Sweden, and Belgium, with 30 per cent. of the consumption of Denmark, Germany, and Holland. The Sun Gas Company, now widely known as the Alby United Carbide Factories, Ltd., and their able Board of Directors, Mr. Albert Vickers, Sir Vincent Caillard, Mr. A. E. Barton, and others, took a leading part, with the co-operation and assistance of the Societa Generale of Rome, in the promotion of the North-Western Cyanamide Co., the Alby Company undertaking the erection of a new factory adjoining to that of the North-Western Company to supply them with the requisite carbide. These works, erected at Odda, which is situated at the head of the beautiful Hardanjer Fjord (Figs. 9 to 11), you will see in the accompanying picture, which shows the carbide works and the adjoining nitrolim works, which are the largest at present constructed. The capacity of the cyanamide works at present is 12,500 tons of nitrolim, and is laid out so as to be eventually enlarged to 50,000 tons. The nitrogen is produced by the largest Linde pump ever erected, with a capacity of 375 cubic metres (13,244 c. feet) per hour, and the latest electrical furnaces are there installed. The author wishes to point out here that the works at Odda, which produce 2,500 tons of nitrogen, only employ from 5,000 to 6,000 kw., whereas from the statement of Mr. Eyde[1] it appears that in the works at Notodden, in Norway, for the preparation of an equivalent amount of nitrogen in the form of nitrate of calcium, 25,000 kw. are required.

In order to complete the review which the author has made of the works already erected for the preparation of nitrogenous fertilisers, it should be stated that the allies of the British in the Far East, the Japanese, are erecting in the south of the Kinskzu Island a works capable of producing 4,000 tons per annum, so that the manufacture of the new fertiliser will soon be localised all over the world.

At the end of the present year works for a total production of over 45,000 tons of nitrolim will be in full swing, and in the course of next year there will be a correspondingly large increase in the means of production of this product.

Though these figures may appear relatively high, they are quite diminutive in comparison with the continual increase in the demand for nitrogenous food for our agriculture, which in Germany alone at the present time shows an annual increase of 15,000 tons of nitrogen, which would, in the form of nitrolim, require a production of 75,000 tons.

It would be an error to assume that the competition of calcium cyanamide on the fertiliser market with Chili saltpetre, sulphate of ammonia, or Norwegian saltpetre can take on the character of a war of annihilation, as was the case with artificial indigo in respect to the natural product. On the contrary, Industry and Agriculture will welcome increasingly large supplies of nitrogen, tending to prevent the rising in the prices of the nitrogenous foods required for the development of plant life.

It will be an especial satisfaction to you, gentlemen, to be assured that just at the present juncture discoveries in the field of electrochemistry have made it possible to succeed in the attempt to supply vegetation with its most valuable food, and that in the future the increasing demands for this form of nutrition by agriculturists can be satisfied, and mankind will, for the future, be able to manufacture unlimited bread and strength.

[1] Extract from the *Archives of the Deutschen Landwirtschaftsrats*, 31st year, 1908.

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APPENDIX NO. I.

SOME COMPARATIVE RESULTS OF THE APPLICATION OF "NITROLIM" TO CROPS.

Spring Wheat.—Manuring experiments carried out by Professor Vincenti, of Ancona.

		Cwts.
I. Manure applied per acre, non-nitrogenous ...	superphosphate	4·78
	potassium sulphate	1·59
Non-nitrogenous manure as above, plus nitrogenous	sulphate of ammonia...	0·79
	Chili saltpetre...	0·40

Yield per acre : Grain, 9·56 cwt. ; straw 18·01 cwt.

See Fig. 12.

II. Non-nitrogenous manure applied same as above—

Plus nitrogenous nitrolim ... ... 1·36 cwt.

Yield per acre : Grain, 9·56 cwt. ; straw, 18·17 cwt.

See Fig. 13.

Winter Wheat.—Manuring experiments carried out by Professor Wagner, of Darmstadt.

III. Average of three years' crops in parallel experiments on areas of one hectare each, and identical applications of nitrogen.

YIELD PER ACRE IN CWTS.

	No Manure.	Chili Saltpetre.	Sulphate of Ammonia.	Nitrolim.
Grain	10·20	16·77	16·34	16·89
Straw	20·64	37·21	34·43	35·06

PROFIT PER ACRE COMPARED WITH UNMANURED.

	£	s.	d.
With Chili saltpetre	2	4	6
With sulphate of ammonia	2	5	4
With nitrolim	2	19	1¼

See Fig. 14.

IV. *Winter Rye.*—Manuring experiments carried out by Professor Wagner, of Darmstadt.

YIELD PER ACRE IN CWTS.

	No Manure.	Chili Saltpetre.	Sulphate of Ammonia.	Nitrolim.
Grain	7·01	15·38	15·30	15·06
Straw	12·51	26·86	28·61	26·38

PROFIT PER ACRE COMPARED WITH UNMANURED.

	£	s.	d.
With Chili saltpetre	1	11	11½
With sulphate of ammonia	2	6	11¾
With nitrolim	2	5	8¾

See Fig. 15.

V. *Oats.*—Manuring experiments carried out by Professor Wagner, of Darmstadt.

YIELD PER ACRE IN CWTS.

	No Manure.	Chili Saltpetre.	Sulphate of Ammonia.	Nitrolim.
Grain	6·13	13·31	13·15	13·31
Straw	15·38	23·43	23·39	25·18

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PROFIT PER ACRE COMPARED WITH UNMANURED.

	£	s.	d.
With Chili saltpetre	1	2	8
With sulphate of ammonia	1	4	3½
With nitrolim	1	9	1¾

See Fig. 16.

VI. *Indian Corn.*—Manuring experiments carried out by Professor Menozzi, of Milan.

COMPARISON OF EQUAL QUANTITIES OF NITROGENOUS MANURES—YIELD PER ACRE IN CWTS.

Manure Used.	Grain.	Stalks and Leaves.
40 per cent. sulphate of ammonia ... 60 per cent. Chili saltpetre	28·61	61·76

See Fig. 17.

Nitrolim	29·25	57·78

See Fig. 18.

VII. *Potatoes.*—Manuring experiments carried out by Professor Steglich, of Dresden.

Manure containing 67¼ lbs. of nitrogen per acre in the form of Chili nitrate, sulphate of ammonia, and nitrolim was applied. Preliminary manuring consisted of 44¾ lbs. phosphoric acid in the form of 18 per cent. superphosphate and 44¾ lbs. of potassium monoxide in the form of potassium chlorate, and besides the equivalent amount of calcium cyanamide 12 cwt. of carbonate of lime were added.

	With Preliminary Manures.	Chili Saltpetre.	Sulphate of Ammonia.	Nitrolim.
Cwts. per acre	40·80	48·61	43·83	46·86

See Fig. 19.

VIII. *Sugar Beet.*—Manuring experiments carried out by Professor Strohmer, of Vienna.

Preliminary manuring, per acre ... { 468 lbs. superphosphate. 224 lbs. of 40 per cent. potassium salts.

Nitrogenous manures, per acre ... { 1·35 cwt. sulphate of ammonia. 1·78 cwt. Chili saltpetre. 1·38 cwt. nitrolim.

CROP IN CWTS. PER ACRE FROM THREE PARALLEL EXPERIMENTS.

	No Manure.	Chili Saltpetre.	Sulphate of Ammonia.	Nitrolim.
Roots	215·96	278·13	255·41	286·49
Sugar	36·10	47·43	43·72	50·08

See Fig. 20.

APPENDIX NO. II.

GENERAL DESCRIPTION OF THE WORKS OF THE NORTH-WESTERN CYANAMIDE COMPANY, LIMITED, AT ODDA, NORWAY.

As the works of the North-Western Cyanamide Company are the largest of the kind so far erected it will be of interest to give some details in connection therewith.

Site.—This was chosen because of its proximity to one of the more abundant

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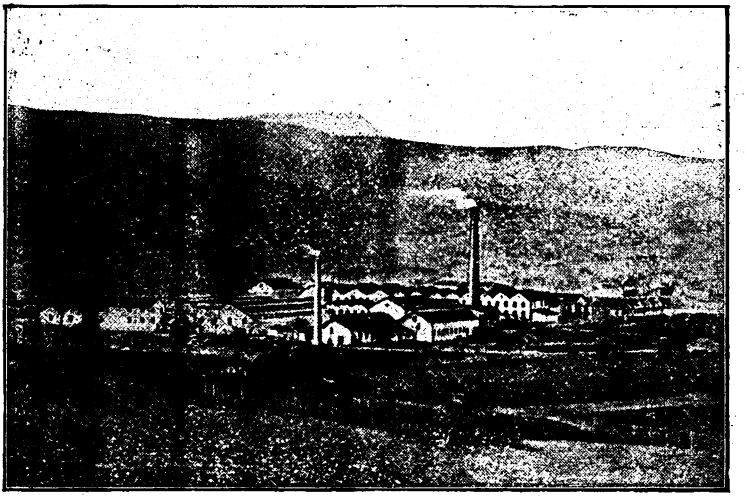

FIG. 4.—Piano d'Orte. General View of Works.

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Odda Village. Cyanamide Works. Carbide Works.

FIG. 9.—Odda. General View of Harbour, Village, North-Western Cyanamide Works, and Alby United Carbide Factories' Works.

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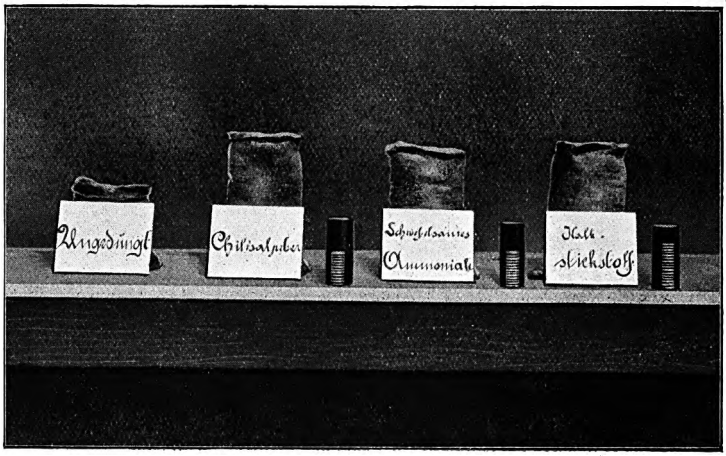

Without manure. Nitrate of soda. Sulphate of ammonia. Calcium cyanamide (nitrolim).

FIG. 14.—Comparative Results on Winter Wheat (Professor Wagner).

Without manure. Nitrate of soda. Sulphate of ammonia. Calcium cyanamide (nitrolim).

FIG. 15.—Comparative Results with Winter Rye (Professor Wagner).

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Without manure. Nitrate of soda. Sulphate of ammonia. Calcium cyanamide (nitrolim).

FIG. 16.—Comparative Results with Oats (Professor Wagner).

FIG. 17.—Indian Corn. With 10 per cent. Nitrate of Soda and 60 per cent. Sulphate of Ammonia.

FIG. 18.—Indian Corn with Nitrolim.

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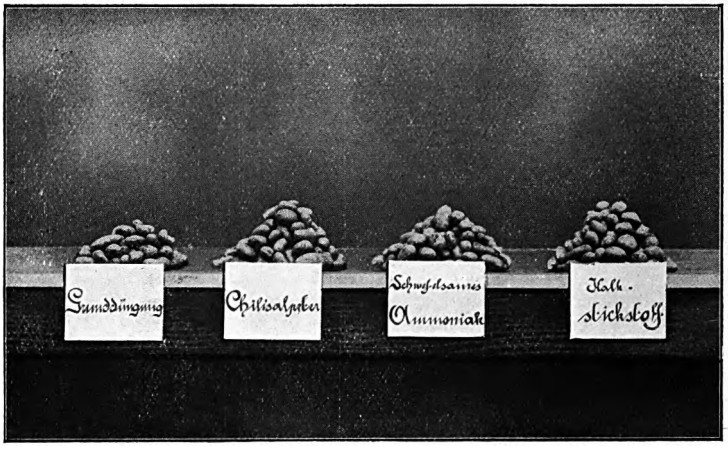
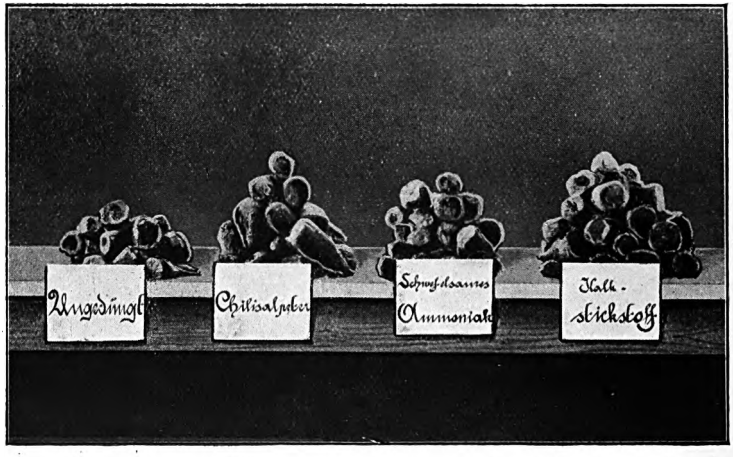


Fundamental manuring. | Nitrate of soda. | Sulphate of ammonia. | Calcium cyanamide (nitrolim).

FIG. 19.—Comparative Results with Potatoes (Professor Steglich)



Without manure. | Nitrate of soda. | Sulphate of ammonia. | Calcium cyanamide (nitrolim).

FIG. 20.—Comparative Results with Sugar Beet (Professor Strohmer).

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and less expensive sources of water-power to harness in Norway, situated in the valley of Tysse, between six and seven miles from the southern end of the Hardanger Fjord, and because suitable level land of sufficient extent for factory purposes existed abutting on the fjord to the east and south of the village of Odda.

Power.—The harnessing of the natural water-power available in the Tysse Valley under agreement with the Alby United Carbide Factories, Limited, was undertaken by the Norwegian Tyssefaldene Company some two years ago. This Company also provided the land adjoining the village of Odda now occupied by the two companies. The power is derived from the last of the small chain of lakes in the Tysse Valley connected by the Tysse River, and fed from glaciers situated some ten miles from the eastern edge of the Hardanger Fjord. This lake is supplied from several lofty natural falls, the chief of which is the well-known Skjœggedalsfal. The water for power purposes is taken at about 40 ft. under the surface of the lake at its lower end, where a drowned dam has been constructed, enters a tunnel some three miles in length driven through the intervening hills, and is delivered to a series of 6-ft. pipes laid on the surface of the cliff overhanging the fjord.

The generating station is built at the fjord level where there is an effective fall of 1,350 ft. upon the turbines. The permanent works, such as the tunnel, &c., are constructed for an eventual output of 80,000 electrical horse-power, but the present installation is for the delivery of a quarter of that amount.

Area Occupied by the Works.—The North-Western Cyanamide Works and those of the Alby United Carbide Factories, which supply the former with the raw material for the manufacture of their "nitrolim," occupy an area of some 34 acres exclusive of land on which their respective workmen's villages are erected, the works of the N.W.C. Company occupying from 6 to 7 acres.

Output.—The cyanamide works are designed for a yearly output of some 12,500 tons of a product testing between 20 and 22 per cent. of nitrogen. The carbide works are intended for an initial output of over 30,000 tons, and both works are laid out so as to be readily and progressively extended to four times their present capacity.

Buildings.—The main buildings of the cyanamide works occupy an area of 38,000 sq. ft., and consist of a suite of buildings comprising the carbide crushing house of three storeys, the electric furnace-room, the cyanamide crushing house of two storeys, the storage hoppers, with the cyanamide aerating-room on top with a storage capacity of some 8,000 tons, the packing-room, with the following isolated additional buildings: the Linde house, the transformer house, the repairing shops and store, and the drawing and general offices and laboratory.

Works Connections.—An electric tramway connects the carbide and cyanamide works and places them in communication with an extensive store at the export wharf, where two large ocean-going steamers can be berthed at once. The carbide works possess in addition an import quay, situated on the east side of the Odda River and connected with their works by an overhead cableway, by means of which the supplies of coal and limestone are delivered at the kilns, and the Cyanamide Company possess a short-length cableway connecting the furnace-rooms of the Alby Company with the upper story of the carbide crushing-room.

Manufacturing Process.—The carbide broken into lumps received from the carbide works is delivered on the floor of the upper story of the carbide crushing house. There it is fed into a first set of crushers, traversing an intermediate set of crushers on the first floor, and thence passes through a double set of mills, where it is ground to the degree of fineness required.

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The whole of these operations are effected automatically with a special plant, which is entirely air-tight.

From the fine grinding mills the carbide powder falls into a closed hopper under floor-level, from which the automatic lifting and conveying machinery delivers it into the furnace-feeding hoppers. The carbide power is then delivered into the recipients for the electric furnaces, of which there are 196 in the furnace-room, constructed for 300-kg. charges. These recipients are lifted and transported by an overhead electric traveller, and dropped into their respective furnaces in the furnace-room. The lids are then put on, fastened down, and rendered air-tight. Nitrogen gas is admitted under pressure. The alternating current is switched on, and the temperature of the contents raised to some 800° to 1,000° C. The whole process of converting the carbide into cyanamide takes on an average forty-five hours, including cooling.

The movable recipients are lifted out, and their contents when cool are delivered into a double set of mills in the cyanamide crushing-room, where they are once more reduced to a fine powder, which falls into hoppers below floor-level, and is lifted and delivered at the height of about 60 ft. on the floor covering the storage hoppers. Here it is fed into long, slow-moving conveying worms, over which is a trunking through which a current of air passes, travelling in the opposite direction to the conveyers. From the aerating conveyers it is distributed and dropped through openings into the storage hoppers, which are arranged on the unicellular system. From the hoppers the cyanamide is drawn, when required, through central horizontal sluice openings at the bottom of the hoppers communicating with conveyer pipes provided with endless worms, delivering into hoppers, from which it is lifted and fed into the tanks supplying the automatic weighing and sack-filling machines in the packing house. The whole of the plant above described has a maximum capacity of some 30 tons cyanamide per working day.

The most important auxiliary building is the Linde house, where a complete plant duplicated in all essential parts for a production of 375 cubic metres of practically pure nitrogen is installed. This plant is too well known to require description, but it embodies all the latest improvements which the accumulated experience of many years has taught the patentees and makers to be desirable. The nitrogen as generated is distributed through control metres to the various plants using it throughout the works without intermediate storage. There are also separate houses for the oil-cooled transformers (English make) of the total capacity of some 2,000 kw., which transform the current delivered by the generating station from 11,000 volts to the working pressure. The repairing workshop and store is provided with a smithy and a complete plate-bending, riveting, and cutting plant for the repair of the electrical furnace and various machine tools. The offices and laboratory are a large and convenient building of two storeys, with rooms for the manager, chief chemist, &c., on the upper floor, and are adjacent to a similar building belonging to the Alby Company at the road entrance of the works.

The workmen's village is situated on the west side of the works at about half a mile distance, and accommodation is provided there for some forty families. Separate buildings for the accommodation of the other members of the works staff and foremen are also provided.

DISCUSSION.

Mr. Henry E. P. Cottrell said he could add little to what Dr. Frank had said. He was pleased to be able to report that the Odda works of the

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North-Western Cyanamide Company were starting operations that very day, and he thought that they would be able to supply all the nitrolim required at present within the sphere of operations reserved to their Company. Of course it was difficult to get the British farmer to use new manures, but they had the support of the scientific agriculturalists, and they also had the support of those who best understood how to make the value of new manures understood by the British farmer. He believed that artificial nitrogenous manures had come to stay, for one reason because they were alkaline, and the ordinary nitrogenous manures were acid, and if applied constantly induced so-called sickness in the soil which the alkaline manure removed.

Mr. Walter F. Reid congratulated the Society on having heard such an admirable Paper from Dr. Frank. He himself was much interested in the subject, having, during the last two years, carried out some tests on nitrolim. He had found that its value as a manure depended largely on the nature and state of the soil. For example, a sandy soil deficient in clay was too light for it, and it needed a certain amount of moisture to make it useful. It was therefore necessary that it be applied under suitable conditions.

With regard to its use in explosives and in smokeless powder, he had made some small-scale experiments, and had found it decidedly efficient in slowing down the explosion—perhaps rather too efficient. There was a distinct reduction in the flame and a cooling down of the gases. It was somewhat strange that a compound of nitrogen could be used to lessen the activity of explosives, themselves nitro-compounds.

The uses of nitrolim as a raw material for the production of other chemicals, some of which were at present rare and expensive, should not be lost sight of, and on this account alone chemists should feel greatly indebted to Dr. Frank, to whose enterprises he wished every success.

Dr. H. Borns hoped that the author would be able to add some information concerning electrical features. The diagrams and views did not explain any details. How long were the carbide and nitrogen heated together? The electrical furnaces installed at Odda were apparently very small units arranged in a good many rows; could Dr. Frank tell them anything about the materials of the furnaces and their operations, and about the electrodes? When Mr. P. A. Guye had lectured on the fixation of atmospheric nitrogen before the Society of Chemical Industry two years ago, Dr. N. Caro had stated that the cost of fixation would approximately be the same for the three processes, the Birkeland-Eyde, Guye, and Frank-Caro processes; did the figures then given still hold?

Dr. J. A. Voelcker (Royal Agricultural Society of England) defended the British farmer in regard to the charge of conservatism and prejudice which had been made against him by the author of the Paper and by Mr. Cottrell, these having been put forward by them as constituting the principal bar to the utilisation of calcium cyanamide. The farmer, he (Dr. Voelcker) thought, was very wise to suspend his judgment. What were the circumstances? Here was a material, the claims of which were strongly advocated; but if he applied for it, the farmer could not as yet be supplied with it, nor was he told what it would cost him. Throughout the whole Paper which they had heard read that evening there was no statement whatever as to where calcium cyanamide could be obtained, what the cost of manufacture was, or what the price to the farmer was to be. Could they, then, be surprised that he was not prepared to abandon the use of nitrate of soda or sulphate of ammonia for this new material? The farmer knew what these latter manures could do for his farm, and he knew what the nitrogen cost him per unit in them. If the advocates of calcium cyanamide could show him that

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he would get equally good results while purchasing the nitrogen at a lower cost per unit, they might be sure that he would not be slow to take it up.

That calcium cyanamide was a perfectly good and useful material to employ had been shown already by experiments made with it. He himself had employed it, experimentally, on the Woburn Farm of the Royal Agricultural Society. There was no reason why it should not do well, but the whole question resolved itself into one of cost. Was the nitrogen to be procurable at a cheaper rate than in the form of nitrate of soda or sulphate of ammonia? Until the advocates of calcium cyanamide could satisfactorily answer this, and also could tell the farmer where he could obtain it on a commercial scale, and not merely in experimental quantities, it was hopeless to look for any advance and unfair to attribute this lack to the prejudice of the farmer.

That the new material was any better than other nitrogenous materials, nitrogen for nitrogen, or better than its rival, calcium nitrate, he did not believe. Indeed, there were drawbacks to its use, as shown in the difficulties found in mixing it with superphosphate and other manures, and in the tendency for it to lose nitrogen on keeping. Here again the whole matter resolved itself into a question of relative cost of production, and the price at which calcium cyanamide could be put on the market.

In the Paper mention had been made of other uses to which calcium cyanamide could be put. One of these was the manufacture of sulphate of ammonia. But it was clear that, for this to succeed, the calcium cyanamide must be capable of being produced at a considerably less cost than the sulphate of ammonia, and it had not yet been proved that this could be done.

Much the same was true of calcium nitrate, a material which was not yet obtainable commercially, and for which no market price was quoted. And when the farmer found matters in this position, he could hardly be blamed that he did not show himself enthusiastic over this and other new discoveries, but that he preferred to wait until he knew what they were going to cost him.

Mr. W. Murray Morrison also hoped that more information would be forthcoming regarding cost of production and power absorbed in the various stages of the process, together with a description of the plant employed. He asked whether it would be possible to make the cyanamide directly from the raw materials in one operation, instead of having first to make carbide, cool it, crush it, and by a second process make the cyanamide. The exothermic nature of this second process apparently rendered the power absorbed very small, but it was obvious that a direct process would reduce the power, the labour, the capital expenditure, and other charges. He also asked whether a carbide of lower purity than that necessary for lighting purposes could not be employed. If so, the raw materials might be of a lower and cheaper quality, and the power absorbed by a lower grade carbide would be much less, the energy and the grade not following in direct ratio. The output mentioned on page 108, namely, 2 tons of carbide per kw. year, would seem to indicate a somewhat lower quality than the English standard carbide used for the production of acetylene.

Did the author think that there would be sufficient demand for all the product in the market when all the works mentioned in the Paper were producing to their utmost capacity? He thought that the heartiest congratulations were due to the author's father, and others associated with him, for the wonderful development of the cyanamide industry in so short a space of time.

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Mr. H. L. F. Vogel asked what the effect would be if a charge of carbide were not completely saturated with nitrogen. Would there not be danger of acetylene being evolved if the powder became moist?

The percentage of calcium oxide present in the cyanamide seemed very high. Was it due to oxygen being left in the nitrogen? What was the degree of purity of nitrogen made in the Linde apparatus?

Mr. Leon Gaster, in drawing attention to the statement of Dr. Frank that the Birkeland-Eyde process apparently required about four to five times as much electrical energy to produce a ton of nitrogen as was necessary in his own process, asked whether he was prepared, to give information on the following points: what proportion the cost of electrical energy bore to the total cost of production, how the cost of the various items, such as calcium carbide, and other materials employed, was distributed, and how they would influence the actual cost of cyanamide.

In the Birkeland-Eyde process, it appeared that the cost of the electrical energy formed the most important item. It was probable that, in the case of Dr. Frank's process, the cheaper the carbide was obtained, the lower would be the price of the cyanamide.

The Chairman thought the Society were very fortunate in having such an interesting Paper as that to which they had just listened, and was sure that members were extremely obliged to Dr. Frank for coming over from Berlin to read this very valuable Paper. From an agricultural point of view the "fixation of atmospheric nitrogen" was of the very first importance, and although there was the process of Birkeland and Eyde, there was room, as the figures which Dr. Frank had placed before them showed, for a very large and increased output of nitrogenous products. There was no doubt cyanamide had come to stay. The inventors were not to be blamed for being sanguine, and it was to be hoped that the product would be found to be of very great value to the agriculturalists. At the same time, they must be prepared to meet criticism, and this criticism would have to be disarmed by actual experimental demonstration. He thought it was all to the good that the agriculturists should be rather critical, because this was better than receiving the new invention with open arms and then finding out that it was not all that it claimed to be. A point that interested him very much was the large number of chemical products which it had been found possible to prepare using cyanamide as a starting material. He was sorry that Dr. Frank had been unable to tell them more about the new electric furnace, and hoped that it would not be long before he was in a position to give them the information which they desired.

Dr. A. R. Frank: In reply to the questions of Dr. H. Borns, Dr. Frank replied that he regretted not being able to give at the time exact information with regard to the new electric furnaces which were being used at Odda for the manufacture of calcium cyanamide. He hoped, however, soon to be able to give the desired information, and he could already say that the method of working the furnaces was, like the carbide process, thermal.

Since the lecture of Prof. P. A. Guye before the Society of Chemical Industry two years ago, on the fixation of nitrogen in the form of cyanamide, substantial improvements and simplifications had been effected, so that the price estimated by Prof. P. A. Guye respecting the manufacture of cyanamide has now been considerably lowered.

Dr. J. A. Voelcker raised a very important question from the point of view of sales of calcium cyanamide—*e.g.*, the sale price. He (Dr. Frank) was only aware of the price which was asked for nitrolim in Italy and Germany. This was at the present time 10 to 20 per cent. lower than that

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for corresponding amounts of nitrogen contained in sulphate of ammonia or nitrate of soda. At this opportunity he would like to point out that the price for Norwegian calcium nitrate in Germany was higher than for the corresponding amount of nitrogen contained in Chili nitrate. He was pleased to learn from the statement of such a high authority as Dr. Voelcker that as a fertiliser nitrolim behaves as well as nitrate of soda and sulphate of ammonia, and that, as already asserted, the price of the material would be decidedly lower than that asked for other nitrogenous fertilisers, and he confidently expected that the English farmer would willingly consume the new fertiliser in large quantities. The difficulties already pointed out by Dr. Voelcker with regard to the mixing of nitrolim with superphosphate might, as stated in the lecture, be considered as solved, and he referred again to the interesting and conclusive trials made by Dr. Hall in this direction. Losses in the percentage of nitrogen contained in calcium cyanamide, which Dr. Voelcker had referred to, had been proved by conclusive experiments to be non-existent. The decrease noticed earlier resulted from the increase in weight, but this difficulty also had been overcome by selecting special raw material and methods of packing.. The regrettable fact pointed out by Dr. Voelcker, that nitrolim was not yet on the market in England, would soon be overcome by the North-Western Cyanamide Company, who would be able to furnish all the quantities required by the English farmer at no late date.

In reply to Mr. Morrison's question, he must say that the experiment of preparing calcium cyanamide from the raw materials—lime and coal—had been carried out on a large scale for a number of years. Furnaces of a capacity of 500–600 kw. had been employed, but succeeded only in producing a 10–11 per cent. nitrogen product against that containing 20 per cent. and over yielded by the indirect method in employing carbide of calcium. The amount of power used in the direct process was originally not less than that required for the preparation of carbide and its subsequent nitrification, but, on the contrary, was even higher. The cost of labour and apparatus for the direct process was not more favourable than that required for the indirect process, and this the more so when the considerable disadvantage ensuing on the production of a low percentage product as compared with a high percentage product was considered.

Notwithstanding this, the former method had not been entirely abandoned; but it would take up too much time at this stage to enter into particulars of the trials made and the resulting conclusions. The quality of the carbide used in the preparation of cyanamide was essentially the same as that employed for lighting purposes as made at all the good European works, which, as stated on page 108, yielded 300 litres of gas per 2 tons of carbide per kilowatt per annum, and, in addition, satisfied the normal standard of carbide lighting. So long as the carbide works installed for the production of carbide did not give up their claim, under certain circumstances, to manufacture carbide for lighting purposes, it would appear that to reduce the quality of the raw materials would render it unmarketable, although such a reduction for the purposes of cyanamide could undoubtedly be effected. It could not at present be decided whether the demand for nitrolim would embrace the production of all the works. When, however, one considered the steadily increasing demand all over the world for nitrogenous fertilisers, one must become convinced that many times the present anticipated production of nitrolim would find a ready market without the least difficulty, without taking into consideration the fact that at some time the Chili nitrate supply must become exhausted.

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In reply to the questions of Mr. H. L. F. Vogel, Dr. Frank said that an arrangement was now in use in all the large works to prevent nitrolim coming into the market containing carbide which would yield acetylene, or which had been damaged in course of manufacture.

The nitrogen made by the Linde process attained usually a purity of 99·8 to 100 per cent. If, through any accident or during storage while being rectified, some oxygen happened to remain in the nitrogen, it would be absorbed during the transformation of the carbide.

Concerning the remark of Mr. Leon Gaster, that the consumption of power for the preparation of equal quantities of nitrogen by the Birkeland-Eyde process was from four to five times as large as that required by the calcium cyanamide process, no objection could be raised. The proportionate cost of power to the entire cost of the preparation of calcium cyanamide depended essentially on the cost of power available for the manufacture of the carbide, as the cost of power for milling and grinding of raw and manufactured materials was only an unimportant item. On the assumption that the average cost of electrical power available at the carbide works was from £2 to £2 10s. per h.p. per annum, the cost of the carbide would amount to about 60 per cent. of the whole cost of preparing calcium cyanamide.

By the Linde process the cost of nitrogen amounted to about 4s. 10d. per cubic metre. It was owing to these conditions that the cost of power and raw materials for the preparation of carbide exercised the greatest influence on the cost of calcium cyanamide.

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RECENT DEVELOPMENTS OF THE KJELLIN AND RÖCHLING-RODENHAUSER ELECTRIC INDUCTION FURNACES.

By J. HÄRDÉN.

(*A Paper read before the Faraday Society, June 23, 1908, Professor A. K. Huntington, Vice-President, in the Chair.*)

The object of this Paper is to discuss the rapid development of the electric induction furnace during the last two years. Before proceeding to discuss the practical improvements in detail, it will be interesting to touch upon one or two novel points of a purely physical nature. We will consider one which will be of general interest—

The "Pinch" Effect of an Electric Current.

Many people experimenting with electric arc and resistance furnaces have observed that when a current is passed through a bath of molten metal or electrolyte the current density cannot be raised to a very high limit without distorting the bath. If the current density is raised to a certain point, it is plainly seen that the metal carrying the current contracts violently, or, in other words, becomes pinched, the effect of which is that the metal on either side of the pinch swells up above the average level of the bath. If the current is still increased, the pinch effect becomes so complete as to actually cause separation in the bath, thereby breaking the current circuit and causing a violent flash, together with rapid volatilisation. This is only a momentary effect, as the separate parts immediately flow together again, closing the circuit, when the same phenomenon repeats itself. Thus it was found impossible to pass an unlimited amount of power into the bath, although one might be well below the boiling point of the metal. The explanation of this pinching is quite obvious. We have only to remember that conductors carrying current in the same direction have a mutual attraction for each other, and if we consider that the molten bath consists of an infinite number of elementary paths of current, it is natural that, as each one is attracting the paths in its immediate neighbourhood, there must be a tendency to compress the full section of the bath. If now, therefore, the bath is slightly contracted at any one spot, the current density will here be raised and the pressure will increase until finally the bath becomes so pinched that an actual break in the circuit may take place. Of course, this is only momentary.

Correspondents of the technical papers have discussed this question, and the point has been raised whether this phenomenon can also be observed in the induction furnace. Theoretically it is obvious that it should, for although the induced current is an alternating one, it has for a given moment of time the same direction in each part of the path.

We have taken observations under working conditions in a 60-kw. Kjellin furnace erected in London for experimental work. A small charge of pig-iron, consisting of about one-third of the full capacity of the furnace, was placed in the bath, and a current of 20 kw. was employed. As soon as the

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charge was fully liquid the pinching effect commenced, and the metal was seen to contract at a certain spot, raising the level of the metal on both sides of the pinch, which was sufficient to break the circuit, causing a flash, immediately after which the metal flowed together again, closing the circuit. The level of the metal immediately on each side of the pinched area rose about 1½ in. above the normal level of the bath. It was found, on examination, that a small piece of slag was burnt into the bottom of the hearth at the point where this phenomenon occurred, thus causing the original reduction of area. Pieces of pig-iron were added to the bath, and as the depth increased the pinching slowly disappeared. It was found that if the original charge was about half of the full charge no pinching effect could be observed.

Another striking feature is the resistance curve of the melt—that is to say, the curve obtained by taking the voltage at constant power across the terminals of the furnace during melting. Supposing we are starting the charge by means of a cold ring of welded or cast iron. Putting on a full load and keeping the kilowatts constant, we first find that the voltage rises above the normal for full load, and as the ring gets hotter the voltage still gradually rises until the ring becomes a bright red heat. From that point a decided drop in the voltage is noticed, although the power is kept constant and the weight of the charge is kept the same. As soon as the ring begins to melt the voltage again rises, but does not reach the same value as before the ring was red-hot. Now let us consider the cause of this result. The furnace is, as you know, nothing but a transformer with a short-circuited secondary. This latter must be placed some distance from the primary, owing to the thickness of the lining, cooling chamber, &c. We therefore have a certain amount of magnetic leakage, not only around the primary, but also round the secondary. The secondary is of iron, with comparatively high permeability, and we have therefore introduced an easy path for the lines of the stray field, hence the increased inductive voltage across the terminals. This is to a certain extent compensated for by the lower ohmic resistance of the ring; but as the resistive coefficient of the latter is such as to increase with the temperature, the total resistance, measured across the terminals, will increase with the temperature, but the power factor will be lower during this period, which shows that it is not only the ohmic resistance that is increased, but also the inductive resistance. This is due to the fact that the permeability of the iron is also increased to a certain extent with the temperature; in fact, it rises very rapidly up to a temperature of about 840° C., when the permeability begins to drop very quickly, and reaches zero at about 920° C. In this interval between 840° and 920° (this figure will vary with various kinds of iron) the inductive resistance is rapidly decreasing, because the easy path for the stray field is checked, and the voltage across the terminals is consequently lowered. But in the meantime the ohmic resistance is steadily increasing, but more slowly than the change in the permeability; therefore, the voltage will again rise, though slowly, until the temperature is reached at which the loss by radiation and the heat introduced balance each other. It may even increase somewhat above this point, owing to oxidation of the charge, but this increase is very slight. This is the explanation why some people were misled into believing that the increase of resistance in iron due to heat was not a straight line curve. (It may, perhaps, not be so, but the effect shown on the furnace terminal is certainly produced in the way stated—which can be proved by the watt- and voltmeter readings.)

Now, turning our attention to the more practical side of our process, we recognise a new feature, which is likely to prove a distinct improvement, viz., the Röchling-Rodenhauser modification of the induction furnace.

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In the original Kjellin furnace some disadvantages are experienced when dealing with material which has to be refined and treated in very large quantities. For instance, when a charge of three tons or more is to be treated, the section of the bath becomes very large, thus causing a low resistance, whereby the power factor is lowered. If we try to increase the resistance by making the ring wider in diameter and of smaller section, the distance from the primary will be greater and the power factor again lower. Thus it becomes necessary to employ a generator of very low periodicity for such furnaces, which is, of course, undesirable. Also the processes of desulphurisation and dephosphorisation are very tedious, as it is difficult to keep the slag sufficiently liquid for such purposes. *Nevertheless, this class of furnace will still hold its own, as it forms an almost ideal crucible steel furnace.* In the case of crucible steel we have seldom to deal with more than one and a half to two tons at a time, and as it does not pay to use impure raw material, no refining is required, but plain melting and "killing," and for this class of work plain induction furnaces can be provided, which will answer very well at 15 to 25 cycles per second. But when it is desired to refine, say, a material smelted from inferior ores and decarburised in a converter, but still containing up to 0·1 to 0·2 per cent. sulphur and 0·05 or more phosphorus, in quantities of five to seven tons, this plain induction furnace would not be so satisfactory.

This was what was required for making rail and other similar steel at the Röchling'sche Iron and Steel Works at Völklingen, Germany, and therefore the engineers at these works, Mr. Rodenhauser and Dr. Schönawa, set themselves to adapt the Kjellin furnace, and so arrived at the "combined furnace." This consists of a transformer furnace with two ring-shaped baths adjacent and communicating with one another, in the case of a single-phase furnace, and three such baths in the case of a three-phase furnace, with a square or rectangular hearth in the centre between the rings, with doors in front and behind, in exterior appearance very much like a Siemens open-hearth furnace; but the principal feature is a heavy secondary winding of copper cables, placed around and co-axial with the primary (one on each leg of the core), surrounded by the rings forming the charge. These copper secondaries, consisting of a few turns only, are connected to conductive plates—they can hardly be called electrodes, for reasons given below—built into the furnace wall, two in front and two at the back for a single-phase furnace. These plates consist of corrugated cast steel plates, and a compound of magnesite, dolomite, and tar is applied firmly over the corrugation. The plates do not conduct well when cold, but as soon as the furnace is charged with molten raw material they will act as a "conductor of the second class," and readily allow the current to pass. Thus about one-half of the power is transmitted to the charge by induction in the rings and the rest of the power through the side plates. As the copper secondary is placed very close to the primary, the leakfield is very much smaller; in fact, three furnaces for one to one and a half tons are now in operation with 50 periods at a power factor of 0·7 to 0·85, a result which could never be obtained with a plain induction furnace of a similar size, in spite of "bifilar" baths and other devices which have been tried. But *this* is not the chief advantage, as the same result may be obtained by other electrical means. A far more important gain is to be found in the metallurgical possibilities obtained with the new design. We know that for carrying out any refining process in steel we need a sufficiently liquid slag and ways and means of handling the same. This is to a certain extent obtained in some "electrode furnaces," where an arc plays between carbon blocks and the slag "blanket." This, however, in some cases, has

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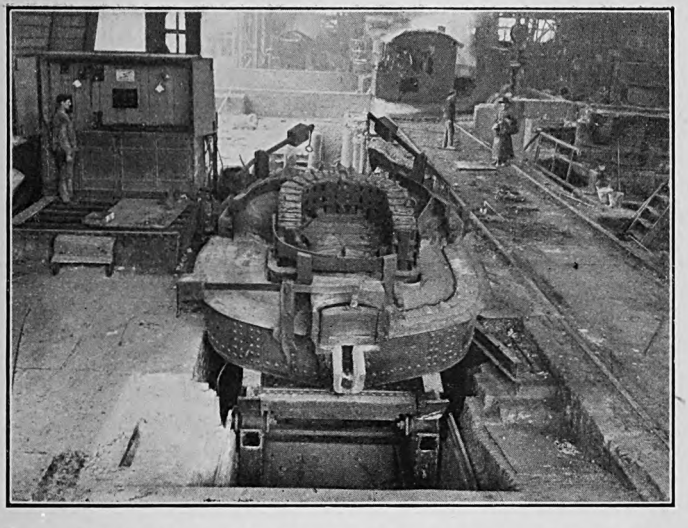

FIG. 1.—The Röchling-Rodenhauser 3-phase Induction Furnace—1 Ton.
(Furnace partly dismantled, showing Rings.)

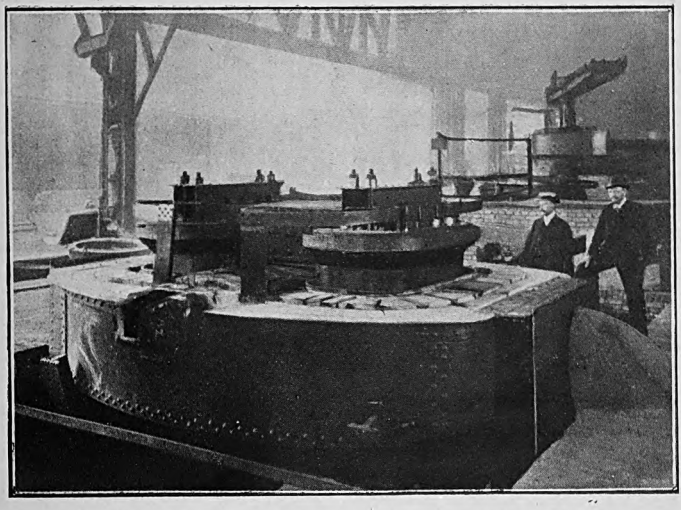

FIG. 2.—The Röchling-Rodenhauser Induction Furnace, Single-phase—
3½ Tons.

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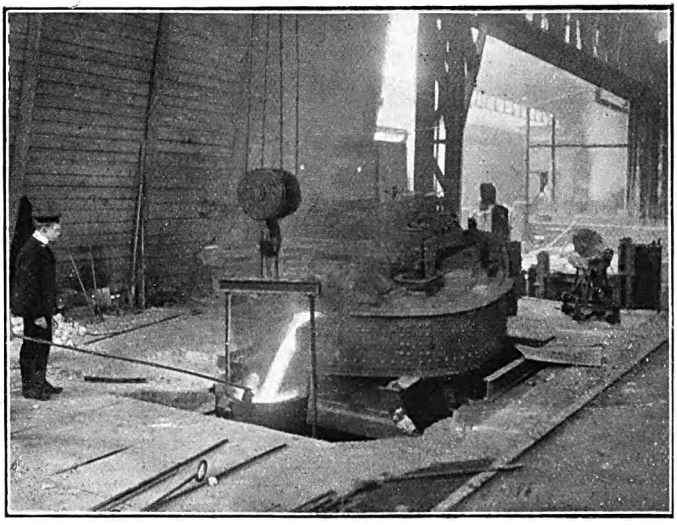
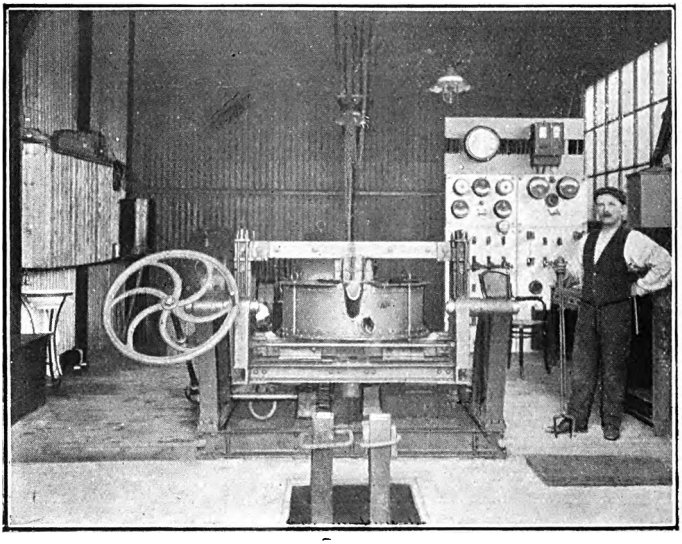


FIG. 3.—The Röchling-Rodenhauser 3-phase InductionFurnace—1 Ton.



60-kw. Experimental Kjellin Furnace—London.

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proved troublesome, the drawback being that the temperature must be extremely and unnecessarily high at the spot where the arcs are playing, which may not be without certain disadvantages to some steels. If we try to dip the carbons direct into the molten metal, we find that they are consumed at once, in such case contaminating the steel, which is, of course, difficult to avoid.

But this is not so in the case of the combined furnace. The conducting side plates before mentioned are of quite a neutral nature ; in fact, some plates, which had been in constant use, day and night, for three months were so little corroded at the end of that period that the loss of the plates, calculated per ton of steel, was hardly determinable. Part of the power is induced in the rings, thus heating the charge, and the rest passes through the side plates, to such an extent only as experience has proved to be necessary in order to obtain a sufficiently liquid slag. The ring-shaped part of the bath is covered with bricks, at a height below the level of the charge in the centre bath. Thus no slag can enter into the rings, and as it is the slag which is injurious to the lining, the rings need hardly any repair during a long run, whereas the rectangular bath in the middle is easily accessible, and can easily be patched out.

The lining is simply calcined magnesite or dolomite, mixed with tar, and stamped in hot.

It has been said that the use of these steel side plates would be equal to a return to the old system of electrodes, with all their disadvantages, but it is evident from what has been stated above that this is not so, as practically no consumption whatever of these plates takes place, and they can hardly be called "electrodes" in that sense of the word.

Let us now follow up the progress of the operation. After the lining is stamped in, the tar is burnt out (either by heating a cast steel ring or pouring a small quantity of pig iron into the hearth), leaving behind a sintered mass, forming a solid brick of basic lining. The pig iron is teemed for treatment in the Bessemer converter, and a fresh charge is given, which is tapped direct from the converter. It is more economical to burn out the carbon and the silicon in the converter, before refining from phosphorus and sulphur. The larger furnace at Völklingen will take a charge of four tons.

Calcined lime is added to form a suitable slag ; this slag sometimes also contains about 6 per cent. of magnesia. In case of need, a small quantity of fluorspar is also added, to act as a flux, but this is not always necessary. Plate scale from the rolling-mill is added for decarborising.

In this condition the slag will take up the phosphorus very readily, after which it is made more viscous by applying cold lime and drawn off through the slag door by a slight tilting of the furnace.

It is essential for a successful dephosphorisation that the charge should be what is called "hot brittle"—*i.e.*, have an excess of oxygen, in order to prevent the phosphorus wandering back into the charge again. After removing the slag which contains phosphorus, ferrosilicon or carbon is added, forming SiO_2 or CO, thus depriving the charge of the oxygen. It has been found that the adding of ferrosilicon will shorten the time of the de-oxidation ; thus, if power is cheap, the cheaper carbon may be employed, and in the case of dearer power it is better to use the ferrosilicon.

As soon as the dephosphorising is effected this first slag is entirely removed, and a fresh slag of lime only is formed, which, when the temperature is raised, acts as a desulphuriser in forming iron sulphide.

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The oxygen is also driven out in this operation, probably partly by combustion of the ferro-silicon (or carbon), whereby the temperature is increased, thus forming calcium carbide, and partly by adding a small quantity of other reactive agents.

After this, the maximum power is applied, in order to drive out the last trace of oxygen, and as soon as no more gas bubbles are seen to leave the charge a test piece is taken out and forged. If too soft for the purpose, some coke powder is thrown in until the right proportions are arrived at. As a rule the operation is finished in one and a quarter to two hours, but if necessary the steel can, without disadvantage, be kept in the furnace for ten hours or more. It is thus possible to treat a material which contains up to 0·1 per cent. phosphorus and 0·1 per cent. sulphur or more so that a product containing 0·006 per cent. phosphorus or less and 0·02 per cent. sulphur or less and from 0·5 to 0·1 per cent. manganese and 0·01 silicon will be obtained.

As to the power consumption, if the furnace is charged with molten material from the converter, the consumption is from 125 to 150 kw. hours per ton of finished material. This, of course, depends upon the quality of the raw material, but 130 kw. hours may be taken as a good average for rail steel.

The finished product is especially distinguished by its great strength, equality, and homogeneity. In fact, rails have been made with a much higher bending and breaking point than ordinary Bessemer or Thomas rails, and these rails command from 25s. to 45s. per ton more than ordinary rails, owing to their greater durability. There is no necessity to give a large quantity of figures as to strength, &c., of this material, but a few may be given below.

ANALYSIS AND PROPERTIES OF ELECTRIC RAIL STEEL.

Exhibited on the Meeting of the Faraday Society.

No.	C.	Mn.	Si.	S.	P.	Tensile Strength. Ton, Square Inch.	Elongation Per Cent. 8 Inches.	Contraction. Per Cent.
1	0·55	0·9	0·30	0·03	0·05	53·2	18·5	31·4
2	0·50	0·9	0·25	0·025	0·05	52·0	19·0	26·7
3	0·55	0·85	0·29	0·03	0·04	52·5	17·0	30·8
				Low Carbon Electric Steel.				
1	0·094	0·30	0·086	0·024	Traces	23·22	36·0	71·5

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RESULTS OF REFINING IN THE COMBINED FURNACE. MECHANICAL PROPERTIES.

CHARGING MATERIAL.						FINISHED MATERIAL.							Tensile Strength. Tons, per Square Inch.	Elongation per cent. Total length 8 inches.	Contraction per cent.
No.	C.	P.	Mn.	S.	Si.	C.	P.	Mn.	S.	Si.	Cr.	Ni.			
1		0·048	0·440	0·137		0·093	0·022	0·420	0·024	0·014			22·5	37·0	70·2
2		0·048	0·496	0·081		0·070	Traces	0·420	0·032	0·010			23·8	40·0	69·3
3		0·064	0·520	0·089		0·152	0·025	0·420	0·024	0·24			31·5	33·5	62·3
4		0·060	0·528	0·084		0·201	0·018	0·435	0·026	0·29			31·0	28·5	51·5
5		0·077	0·580	0·089		0·144	0·022	0·495	0·035	0·31			32·8	31·0	53·2
6		0·042	0·592	0·097		0·334	0·024	0·540	0·024	0·38			39·75	27·5	48·5
7	0·400	0·098	1·050	0·073	0·15	0·397	0·015	0·667	0·020	0·34			41·4	26·0	41·3
8		0·057	0·488	0·105		0·690	0·023	0·347	0·016	0·19			45·2	19·0	32·9
9		0·071	0·420	0·057		0·854	0·016	0·352	Traces	0·31					
10		0·048	0·580	0·121		0·892	0·015	0·376	0·016	0·13					
11		0·049	0·540	0·081		0·928	0·016	0·360	0·019	0·12					
12		0·070	0·450	0·073		0·939	0·016	0·318	Traces	0·22					
13		0·060	0·340	0·105		0·972	0·018	0·300	0·016	0·25					
14		0·085	0·440	0·065		1·00	0·026	0·352	Traces	0·20					
15		0·045	0·460	0·073		1·04	0·012	0·300	0·016	0·16					
16		0·043	0·476	0·057		1·05	0·011	0·330	0·013	0·18					
						Steel Alloys.									
17		0·069	0·464	0·078		0·080	0·015	0·253	0·032	0·14	0·81	4·03	40·3	17·5	46·4
18		0·060	0·460	0·081		0·212	0·016	0·505	0·028	0·26	0·74	2·98	61·5	12·5	23·5
19		0·050	0·500	0·081		0·620	0·025	0·880	Traces	0·79	0·69		65·0	7·0	49·2
20		0·081	0·460			0·750	0·022	0·283	0·016	0·41	1·05		72·1	10·0	23·4
21		0·074	0·540			1·170	0·022	0·320	0·016	0·30	1·60				

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DISCUSSION.

Mr. F. W. Harbord considered the modified Kjellin furnace described in the Paper a useful improvement on the original furnace. He did not, however, see how a 7-ton furnace could make rail steel in competition with a modern converter of 10 to 14 tons capacity, or a 50-ton open-hearth furnace. The electric process, in fact, was really a *refining* process, and should be used as such, either in conjunction with a converter or an open-hearth furnace; this was the most promising future for the electric furnace, in connection with steel manufacture.

He did not think the etched rail sections they had seen proved very much as regards the uniformity of the electric as against open-hearth steel. All rails varied very considerably in this respect. He would like to know whether this steel was actually being used for rails.

As regards the high breaking stress of the material, there was no difficulty in making such steel, containing, for instance, only a trace of phosphorus, provided pure materials were used, as they were here. The induction type of furnace was not, in his opinion, particularly well adapted for impure materials, and its real advantage was, that it worked in a neutral and not an oxidising atmosphere. It was a crucible furnace, in which ton lots instead of pound lots could be made.

He was much interested to find that calcium carbide was produced in the furnace *in situ*. He had seen—he believed in an Héroult furnace—carbide added to deoxidise the bath, with extremely good results.

Mr. E. Ristori said that the title of the Paper gave a wrong impression of the type of furnace the author had described, which was not an induction, but a combined induction and resistance furnace, and it appeared to him from the description that most of the work was done in the resistance portion of the furnace. The induction type of furnace, he considered, was only suitable as a substitute for crucibles, but was not capable of refining steel, viz., of making good steel out of impure raw materials. This could only be done by means of the resistance type of furnace, such as the Héroult furnace, and he noted that the inventors had to fall back on the resistance principle when they wanted to refine steel.

He would like to ask the author if he could give an analysis of the raw materials used and of the finished steel in order to see what amount of refining could actually be done in practice by the type of furnace described.

Dr. H. Borns: We have reason to thank Mr. Härdén for his paper. The recent discussions on the performance of electric iron and steel furnaces, notably in Germany, have helped us to a good deal of useful information, and Mr. Härdén has now made some valuable additions. May I ask a few questions? What was the depth of the metal in the trough when Mr. Härdén observed the pinch effect? I should also feel obliged if Mr. Härdén could explain more fully how the metal is kept at a somewhat higher level in the central portion of the Rodenhauser furnace than in the ring. It is said that the iron will, in the annular trough, assume an inclined position as if it were under the influence of a centrifugal force; the effect is ascribed to the combined action of magnetic stray fields and of gravity. Is the surface always inclined, and does Mr. Härdén accept the suggested explanation? Mr. Harbord has already referred to the part played by calcium carbide in the purification of the steel; Héroult and Eichhoff make a point of the action of the carbide, especially with regard to the removal of the sulphur. Mr. Härdén tells us that the carbide must be formed *in situ*, and that he

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noticed the smell of acetylene. Have we any real evidence of this formation *in situ?*

Dr. Richard Seligman said that as the time was so far advanced he would not detain the meeting longer than to put one or two questions to the author. He had been extremely interested in the author's remarks on the "pinch effect," a phenomenon which was of importance to all of them who had to pass heavy currents through molten conductors, and one which had a habit of cropping up in the most unexpected way. Could the author tell them at what current density the "effect" was observed in the case of molten iron?

The author stated that the "sticky" property of iron was due only to high temperature, and gave as his reason the fact that when fresh metal was added to the bath the stickiness entirely vanished. But was the effect of the added metal merely to reduce the temperature of the bath? Was it not possible that the "sticky" metal was merely diluted by the addition of the fresh metal, or had the author made the experiment of lowering the temperature of the bath by other means in order to see whether the stickiness disappeared in the same way?

Dr. J. A. Harker joined the previous speakers in congratulating the author on the many interesting facts revealed in the Paper. The Gröndel-Kjellin Company had last year kindly presented a small experimental induction furnace, taking some 25 kw., to the National Physical Laboratory. He hoped this would soon be working, they had been obliged to erect a special building to place it in, for it was intended to study in it some of the interesting questions raised by the author—he would instance the increased resistance of iron at high temperatures—and to determine the physical constants of iron and steel and other metals at high temperatures, accurate data which we were so badly in need of.

The speaker also referred to some experiments in which he had noticed the "pinch" effect alluded to in the Paper. In conjunction with Mr. W. A. Price he had attempted to use a resister of molten tin as the heating medium for a bath of fused salts. If the resister were made in the form of a gridiron, the metal being contained in channels machined on the surface of a fire-brick, it was found that at high-current densities, using alternating current of fairly low frequency, severance of the conductor always took place, rendering the method incapable of application. Even with a straight channel, where magnetic effects of the current would be less serious, the slightest irregularity in the shape of the channel holding the metal apparently determined the point of severance. The current densities in these experiments would be from 5,000 to 15,000 amperes per square inch, and the conductors about $\frac{1}{16}$ square inch in cross-section. It was not found possible to employ the method as originally intended.

For experimental purposes it was impossible to overrate the advantage of being able to melt metals and other substances in a neutral atmosphere, such as one had in the induction furnace. The new metallic filament lamps were calling out for such a furnace which could be worked *in vacuo*. Tungsten, for instance, combined with almost any gas that came near it, and a vacuum induction furnace was therefore a necessity. Did the author know whether the Colby furnace, for which American patents were taken out some years ago, was being used for melting platinum and other refractory metals *in vacuo?*

Dr. J. Härdén, replying to Mr. Harbord, said the steel had been used commercially for various purposes, among others for automobile work (samples exhibited). As regards rails, the Prussian State Railways had

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recently ordered considerable quantities for points and crossings, paying some 40 marks a ton more than for ordinary steel. Those who could appreciate this fact would recognise that there must be good reasons for such willingness to pay an extra 40 marks a ton. When discussing the extent to which the steel had been used, it must be borne in mind that the large furnace described was the first of any size built. With reference to the presence of calcium carbide, if ready-made carbide is added to the slag no action takes place (it may even be injurious to the process) provided that the temperature is *not high enough to decompose* the carbide, in which case desulphurisation is observed. The author's theory, however, is that when lime, CaO, is added to the steel while the latter contains an excess of oxygen, a deoxidising material, such as carbon, or, still better, ferrosilicon, also being present, the oxygen then acts upon this substance in a combustive manner, *whereby the temperature is considerably increased.* Therefore, with aid of the carbon present in the steel, the lime is partly decomposed into calcium and carbon monoxide; the free calcium combines instantly with the sulphur, forming calcium sulphide, while a portion of the calcium, at this temperature, takes up some of the carbon present, thus forming calcium carbide, both being found later in the slag. Consequently it is not the carbide *per se* which acts as a desulphuriser or deoxidiser, but its presence is merely *an indicator* that the desulphurisation has actually taken place. It is the ferrosilicon, &c., which deprives the steel of its oxygen, thereby raising the temperature so that the above reaction may take place. Hence also the necessity of excessive heat when trying to desulphurise by means of ready-made carbide, which will have to be decomposed at high temperature; this may certainly be carried out in an arc-furnace, but is to the author's mind a waste of power, The excessive formation of carbide in any steel furnace must be a waste of power, as it is always an expensive process; it is only necessary to form sufficient carbide to indicate that the desired reaction has taken place.

In the case of an arc furnace, with a very high temperature under the arcs, the possibility exists that the deoxidation may be effected by means of lime only (or carbide); *i.e.*, if the lime (or carbide) is decomposed by the heat, part of the free calcium may form calcium sulphide, and, as soon as the critical point is again reached, oxygen may be taken from the steel, re-forming lime together with the calcium present in the slag. Of course, no free calcium will ever be found in the slag after it has been withdrawn from the furnace, as it is oxidised instantly by the atmospheric oxygen.

The above theory is, of course, very difficult to prove, but many observations tend to indicate that it may be right, and it would certainly be very desirable if the matter could be fully cleared up.

Referring to Dr. Harker's remarks, the interesting little furnace at the National Physical Laboratory was the one that had been in use at the Sheffield Exhibition. It would melt 7 lbs. of iron in twenty minutes. It had a power-factor of 78 to 81 per cent., and worked with a frequency of 210, the core being very narrow, as it was especially adapted for melting rare substances.

The Colby induction furnace had been mentioned. In one form of this the windings were outside the crucible, and on this account the power-factor was low. No large furnaces of this type had been built, and the Colby Company was now working in conjunction with the Kjellin Company in America.

He knew of no vacuum induction furnace, but he thought that although considerable mechanical skill would be called for there was no serious difficulty in the making of one. The best vacuum electric furnace he knew of was that of the General Electric Co., U.S.A., designed by Mr. Arsem. In

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this boron carbide had been made and the existence of two carbides had been proved.

Wolfram may be produced in a crucible lined with wolfram oxide.

In reply to Mr. Ristori's remarks, the Kjellin furnace was originally only a melting furnace, but when it was found necessary to refine it was modified to the combination form; but as, generally speaking, two-thirds of the power was inductive—depending on the degree of refining required—and at the least one-half, it was not accurate to call it a resistance furnace. Moreover the electrodes were neutral and unacted upon.

Replying to Dr. Borns, the depth of the bath, when the pinch effect was observed, was about 1¾ to 2 inches. As to the difference in level, this was very slight only, and effected by brickwork, covering the rings and secured by bandage of iron. As regards the level on the surface in a Kjellin furnace, the magnetic forces are tending to drive the metal outward, widening the ring, thus raising the level on the outer wall; but the thermal effect, caused by higher current density in the inner parts, will make it rise still more on the inner wall, where also the slag may be mostly observed.

In reply to Dr. Seligman, the bath section was about 1½ × 2 in. and the current about 9,000 amps., but the density might have been higher, due to the obstruction which started the pinch. The "stickiness" of the metal in the observed cases was certainly due to temperature only, and it was overcome by cooling.

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THE HEATS OF COMBUSTION OF ALUMINIUM, CALCIUM, AND MAGNESIUM.

By F. E. WESTON, B.Sc., and H. R. ELLIS, B.Sc.

(A Paper read before the Faraday Society.)

The values given by various experimenters for the heats of formation of Al_2O_3, CaO, and MgO differ very considerably, as is shown in the following table.

I. $Mg + O = MgO$—

Heat Evolution.		Authority.
148,000 calories	...	Dr. Strauss, *Minet, Production of Al*, p. 209.
143,300 ,,	...	Beketoff.
143,400 ,,	...	*Electrochemical and Metallurgical Industry*, 6–8.

II. $Ca + O = CaO$—

151,900 calories	...	A. Guntz and H. Bassett, jun., *C. R.*, 1905, **140**, 863,864.
131,500 ,,	...	Thomsen (see L. and B.).
145,000 ,,	...	Moissan.
131,648 ,,	...	Dr. Strauss, *Minet, Production of Al*, p. 209.
130,900 ,,	...	Thomsen.

Guntz used pure Ca and formed pure compounds, from which he determined the heats of solution; this, of course, introduces complications, leading to various corrections. Forcrand, using pure CaO from $Ca(OH)_2$ and determining heats of solution, obtained the same value as Guntz (*C. R.*, 1908, **146** 217–220). Thomsen used CaO prepared from calcium nitrate, and Forcrand (*C. R.*, **146**, 217–220) points out that the low value obtained was probably due to impurities; consequently all values based on Thomsen's results will be low (see also *J. C. S.*, Abst. II., **155**, 1908).

Moissan's result was obtained by direct determination of the heat of combustion, and therefore is less liable to error than those results obtained by indirect means.

III. $2 Al + 3 O = Al_2O_3$—

386,988 calories	...	Dr. Strauss, *Minet, Production of Al*, p. 209.
380,200 ,,	...	Thomsen (see L. and B.).
392,610 ,,	...	Richards, *Electrochemical and Metallurgical Industry*, 6–8.

Calculating these results for 1 gram-atom of O, they become 128,996, 126,733, and 130,870 respectively.

On account of the great divergence in the above numbers, experiments were carried out with a view of ascertaining as far as possible which element has the greatest heat of combustion by examining the reducibility of the oxides of aluminium, calcium, and magnesium by the metals Al, Ca, and Mg respectively.

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From the foregoing tables it will be seen that the average value of the heat of combustion of Mg is 145,000 calories, that of Ca is 137,000 calories, and that of Al is 129,000 calories; hence from the theory of greatest heat development Mg should reduce CaO and Al_2O_3, Ca should reduce Al_2O_3 and not MgO, and Al should not reduce CaO or MgO.

Now Goldschmidt (*Minet, Production of Al*, p. 213) has already shown that Al can reduce CaO, and Dr. F. M. Perkin has succeeded in reducing Al_2O_3 by Ca; but it was thought advisable to repeat these experiments in order that a complete comparison could be made between the various reductions when carried out under the same conditions.

Experimental.

Series I. The Action of Al Powder upon Al_2O_3, MgO, and CaO respectively.

The Al powder was the same as that used by the authors in their previous work (see *Trans. Far. Soc.*, vol. iv., 1, 1908). The Al_2O_3 was prepared by ignition of pure ammonia alum. The MgO was made by ignition of precipitated magnesium carbonate, and was heated for some hours in a muffle at 1,000° C. and was in an extremely fine state of division. The CaO was obtained by ignition of marble, finely powdered, passed through a 40,000-meshed sieve, and the resulting powder again heated at 1,000° C. for one hour.

1. $Al_2O_3 + 4\,Al$. This experiment was first carried out by Duboin (*C. R.*, cxxxii., No. 13). The mixture readily reacts with a fuse, forming a blackish-grey product which dissolves in HCl with the evolution of H; it contains, probably, a suboxide of aluminium, but very little nitride.

2. $2\,Al + 3\,CaO$. The mixture, contained in a Hessian crucible, would not react in the cold, even when a fairly large fuse was used; when heated over a bunsen burner for two hours (the bottom of the crucible was at a dull red heat), a fuse again brought about no reaction. The crucible was then placed in the muffle at its hottest part; after two minutes, the crucible then being bright red, action started at the surface and then very rapidly spread throughout the whole mass, giving a somewhat violent reaction. The reaction consisted first of the oxidation of the surface Al by the air, and the heat produced by this reaction, together with the heat supplied by the furnace, brought about the reduction of the CaO by the Al; this reaction appears to us to be endothermic, since it was only possible to bring about the reaction under the conditions stated. The product of the reaction consisted of a hard, black, fused mass, and contained free Ca, calcium aluminate, free Al (and possibly some Al_2O), Al_2O_3, and CaO; it also contained a small amount of nitride and carbide.

Estimation of Free Ca and Al.—The finely powdered substance was treated with cold water and the gas evolved collected and analysed. From volume of H evolved the percentage of free Ca was calculated; a small quantity of C_2H_2 and CH_4 was found present. After treatment with water, HCl was added and the process repeated.

Per cent. free Ca	=	8·3
„ „ free Al	=	6·1
„ „ nitrogen (as nitride)	=	0·375

Hence it is evident that Al powder can reduce CaO at high temperatures, and it is probable that the reaction $2\,Al + 3\,CaO \rightleftharpoons 3\,Ca + Al_2O_3$ is a reversible one and that a stage of equilibrium is reached under the above conditions.

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3. 2 Al + 3 MgO. The reduction could not be brought about even at the highest temperature attainable (*e.g.*, about 1,100° C.); the only change obtained was a superficial oxidation of the Al; the contents of the crucible were otherwise unacted upon.

Hence it appears that the heat of formation of MgO is greater than that of CaO.

Series II.

1. 3 Ca + Al_2O_3. The calcium was first converted into fine shavings in a lathe, and these were then crushed as small as possible in an iron mortar, and that portion which passed through a 120-meshed sieve was used.

The mixture, in a Hessian crucible, would not react in the cold even when a moderately large fuse was used, but on heating with a bunsen burner until the bottom of the crucible was at a dull red heat, a violent reaction took place and the larger portion of the contents of the crucible was ejected. From the way in which the reaction took place it is fair to assume that if calcium powder in a sufficiently fine state of division were employed the reduction would take place readily in the cold, and if air were excluded and sufficiently large quantities of mixture employed, fused Al could be obtained (see also Dr. Perkin, *T. F. S.*, iii., 3, 184). In this reaction the Al produced probably volatilised, and consequently oxidised under the very high temperature obtained, and this may account for the small percentage of Al found and also for Dr. Perkin's failure to obtain globules of metallic Al. The authors intend repeating this experiment under such conditions as to avoid loss, &c.

The presence of free Al was shown by treating the finely powdered product with water until no more gas was evolved, even on heating, and then adding HCl; a rapid effervescence of H took place, and Al was found in the solution. The product contained about 8 per cent. of free Al.

2. Ca + MgO. The mixture, placed in a Hessian crucible, was found to react slowly when the surface was heated with a bunsen burner; the surface Ca ignited, and the incandescence *slowly* spread throughout the mass from the top downwards. On cooling the contents of the crucible were found to be white at the top to a depth of about $\frac{1}{8}$ inch, and then of a deep yellow.

It was thought at first the action was due to reaction of the Ca with the atmosphere forming a small amount of lime and a large amount of calcium nitride. That this was not so was evident from (1) the analysis of the resulting mixture; (2) that the calcium when heated in a crucible by itself under the same conditions only burnt on the surface and remained unchanged below; and (3) a mixture of CaO and Ca when treated in the same manner or even when strongly heated by a Bunsen flame only reacted at the surface.

Analysis of the product gave—

N as nitride	= 5·79	per cent.
Free Ca	= 4·16	„ „
„ Mg	= 0·58	„ „

It was not possible to decide whether the nitride was calcium nitride or magnesium nitride or a mixture of both. But from the large percentage of nitride (about 30 per cent. if calcium nitride) it appears that the atmospheric N plays a great part in the reaction observed.

Series III.

1. Mg + CaO. That Mg will readily reduce CaO in the cold is, of course, well known, this reaction serving for the preparation of argon from the air. A mixture made in the proportion Mg + CaO can easily be fired by a lighted

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match, the reaction proceeding steadily throughout the mass. The resulting product is of a bright yellow colour, and consists chiefly of calcium nitride.

Analysis of product gave—

Ca_3N_2 = 33·65 per cent.
Free Ca = 1·29 „ „
„ Mg = 0·47 „ „

In this reaction, in order to obtain a yield of Ca, air would have to be excluded.

2. 3 Mg + Al_2O_3. This mixture, in a Hessian crucible, easily reacted with a fuse; the reaction was somewhat violent, the mass swelling up considerably. The resulting product was quite black.

Analysis of product gave—

N as nitride = 7·43 per cent.
Free Al = 0·71 „ „
„ Mg = 3·87 „ „

In this reaction, as in the case of Ca and Al_2O_3, it is probable that most of the Al liberated is converted into nitride and some re-oxidised to Al_2O_3.

Although in these experiments, which were only carried out on a small scale (20 to 50 grams), complications arise partly from the interaction of the various hot metals with the air and with the oxides, it is quite evident that both Mg and Ca reduce Al_2O_3 in the cold and also that Mg easily reduces CaO with the formation of the free metal.

It is thus evident that the heat of combustion of Mg is greater than that of Ca, since MgO is not reduced by Al, whilst CaO is at a very high temperature; however, the heat of combustion of Mg is not much greater than that of Ca, since it is possible to cause Ca to interact with MgO; also the heats of combustion of Mg and Ca are much higher than that of Al.

The partial reductions of CaO by Al and of MgO by Ca—probably endothermic reactions—are analogous to the reduction of B_2O_3 by K and Na respectively. Gay-Lussac prepared B by heating B_2O_3 with K to a red heat in an iron tube. Now, the heat of combustion of B to B_2O_3 is given as 317,200 (Troost and Hautefeuille-Watts, *Dictionary*), 314,821 by Roscoe and Schorlemner; whilst the heat of combustion of K to K_2O is given by Beketoff as 97,100 (L. and B.), 86,800 by Rengarde (*J. C. S.*, Abs. II., 156, 1908), and 84,800 (*ibid.*).

Hence $B_2O_3 + 6K = 3K_2O + B_2$ becomes thermally (using average values)

$$-[(316{,}000) - 3(89{,}500)]$$
$$i.e. = -47{,}500;$$

i.e., heat must be supplied; a similar reaction occurs with Na.

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THE INFLUENCE OF CHEAP ELECTRICITY ON ELECTROLYTIC AND ELECTROTHERMAL INDUSTRIES.

By E. A. ASHCROFT, A.M.I.C.E., M.I.E.E., &c.

(*A Paper to be read before the Faraday Society.*)

The industries of electrometallurgy and electrochemistry became commercial only with the invention of the dynamo in 1867.

And to-day we are standing on the verge of greater developments, foreshadowed by the recent rapid increase in the production of such metals as aluminium and sodium in America and Europe, experiments in the electric smelting of iron, developments in steel refining, the success of the lime nitrogen works at Notodden, Norway; the extensive growth of the carbide and, later, of the cyanamide industries in Norway, Italy, and Switzerland, the introduction of a successful lead-refining process, sulphide ore experiments, lead and copper smelting experiments, zinc distillation, and many other promising operations just emerging from the experimental stage.

It is becoming clearer every year that the extent of these developments in the near future will depend on the limits to which the cost of electric energy can be reduced at suitable sites.

For this reason the special influence of cheap energy on electrolytic and electrothermal industries, although not strictly a scientific question, becomes a matter of great interest to this Society.

The large developments at Niagara Falls have familiarised the world with the possibilities of water-power; but they have also brought certain well-defined limitations to light; for it now becomes evident that at Niagara Falls the price of energy to the consumer is not low enough, and never can be low enough, to satisfy the rigid economical demands of many, technically possible, industrial processes which would soon become commercially possible with sufficiently cheap energy.

But if Niagara power is too dear, what chances have the steam, gas, and oil engines' motors which one hears so much about nowadays?

As main generators of energy for the purposes above stated, the answer is that they have no chance at all. For even if absolutely free and regular supplies of fuel were available for such engines (which is certainly not the case) the capital charges, and the upkeep would still bring the cost of the unit of electricity somewhere about the level of the Niagara prices, and still far above the "low-grade limit" which will be inexorably demanded by the coming new industries as a root condition of their being.

I should be inclined to suggest for this "low-grade limit" about £2 per kilowatt year (£1 10s. per horse-power year) and we may at once quite safely assume that no means of producing energy at present known or thought of can touch this limit except one, and that I have designated water-power of Class I.* In some exceptional cases already the price of energy by water-power

* That is to say, those water-powers in which favourable natural conditions enable the development of the power at a very low expenditure of capital.

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has been reduced below that limit. In fixing this limit I, of course, assume that some profit is to be made on the large industries considered as well as on the water-power, not merely the covering of working expenses and capital charges.

TABLE I.

Relative Costs of Electricity Produced from Steam, Gas, Oil, Water (2) and Water (1) for Continuous Loads.

Item.	Steam Engines.	
	Per Kw. Year.	Per H.-P. Year.
	*£ s. d.	£ s. d.
Fuel	4 2 6	3 3 0
Labour	0 11 0	0 8 0
Upkeep	0 13 0	0 10 0
Capital charges	3 0 0	2 8 6
Royalties on rights	—	—
	8 6 6	6 9 6

Item.	Gas Engines.		Oil Engines.	
	Per Kw. Year.	Per H.-P. Year.	Per Kw. Year.	Per H.-P. Year.
	*£ s. d.	*£ s. d.	£ s. d.	£ s. d.
Fuel	2 8 0	1 14 0	4 0 0	3 0 0
Labour	0 8 0	0 6 0	0 7 0	0 5 0
Upkeep	0 16 0	0 12 0	0 16 0	0 12 0
Capital charges ...	3 6 0	2 13 6	2 1 0	1 11 0
Royalties on rights ...	—	—	—	—
	6 18 0	5 5 0	7 4 0	5 8 0

* Varies greatly according to value of bye-products obtained.

Item.	Water, Class II.		Water, Class I.	
	Per Kw. Year.	Per H.-P. Year.	Per Kw. Year.	Per H.-P. Year.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Fuel	—	—	—	—
Labour	0 8 0	0 6 0	0 6 0	0 4 0
Upkeep	0 13 0	0 10 0	0 8 0	0 6 0
Capital charges ...	4 2 0	3 2 0	0 13 0	0 10 0
Royalties on rights ...	0 3 0	0 2 0	0 13 0	0 10 0
	5 6 0	4 0 0	2 0 0	1 10 0

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The undeveloped water-power of the world is still very large; and as a consequence no regular market value has yet been placed upon water rights in public estimation, (except in special circumstances where their market value is at once apparent). I have treated the possibilities of royalty payments as a contingent item in the comparison of costs. This item will, however, find its natural commercial level as industry extends, and the demand for such water-power increases.

The accompanying Table I. of comparative costs of the various available means of producing energy is prepared from many records, and it aims at striking a useful average. Of course it follows without saying that no "average price" can be accurate for all countries, but nevertheless the difference in these figures in different situations is not in fact so great as might at first appear likely, when the division of water-powers into two classes is adopted. The principal difference is a fundamental and striking advantage peculiar to water powers of Class I.

It is not proposed to discuss either steam, gas, or oil engines here, for a glance at the table shows that they are quite out of court in this larger connection which we are considering.

The best practical source of energy "in bulk" to-day is the favourably-placed waterfall, and the second best is a waterfall of Class II., which may also sometimes have the advantage of being obtainable nearer home.

A growing demand for large gas and oil motors, however, is indicated by the state of the markets to-day, a circumstance which is explained by the fact that many operations consuming energy are absolutely bound to be carried out at spots where no waterfall can be obtained. Moreover, in the particular industries which I am considering here quite a large demand may yet arise for gas and oil engines; for there are indications of a tendency to devise apparatus wherein a combined use is made of electrothermal (or electrolytic) and of direct combustion principles. Thus it has been suggested that a charge of iron ore, carbide materials, or similar raw materials, might be heated up by ordinary fuel combustion to nearly the required temperature and made thus to imbibe a large number of necessary heat units at a cheap rate, and then finished off by raising it to final temperature, with the aid of the more expensive electric heat. Such operations could, of course, be carried on economically at sites even nearer to the markets than the cheap water-power sites of which I shall speak presently, and an advantage of some importance might be thus obtained in respect of freights. Also, it is to be noted that in such countries as England and Germany, where there are few or no water-powers of Class I., there will be found a great desire to keep industrial operations as much as possible within the respective countries. For these reasons the gas engine has every chance of encouragement. But the fundamental, unalterable, natural economic conditions of any industry should not be wholly obscured by such considerations.

I am convinced that much larger developments will take place during the next few decades at the first-class water-power sites. Such developments, in fact, are already taking place, and will be limited only by the comparative scarcity of this class of power in the world, and I may add by the false patriotic ideals which sometimes actuate the peoples of the few naturally favoured lands where such powers exist.*

* In Norway at the present time an absolutely unparalleled opportunity is offered to the country for a prosperous era of commercial development such as few countries have ever seen, but the people, though highly intelligent in other respects, have not the power to appreciate it, in virtue of their national selfishness. Instead of rising as one man to meet this great opportunity, they are hampering the develop-

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It is therefore probable that when such causes are removed there will be a reversal of the present exclusive policies, and then foreign capital will be welcomed, even subsidised and encouraged to develop the natural resources of the country. When this takes place I predict for these industries, and for that fortunate land which possesses the water-powers of such exceptional qualities, an immense access of prosperity.

In support of this the following significant figures may be cited :

Although electrically produced heat can probably never compete in cost, unit for unit, with heat produced from coal burned direct, yet the ratio of cost between the two is much lower than is usually supposed, whilst the ratio of efficiency brings the two still more nearly on a level, turning the balance in many cases in favour of greater economy for electric heating.

One pound of an ordinary quality of coal will generate, if burned in a producer and supplied to a modern gas engine, about one electrical horse-power hour, and it will cost at the pit's mouth (at 8s. per ton) ·05d.

This amount of electric energy (one electrical horse-power hour) is equal to 644,544 gram calories of heat energy.

Burned directly to generate heat, one pound of coal will produce approximately 3,000,000 gram calories. Therefore by burning coal, for £1 we may procure a theoretical combustion heat of approximately 15,000,000,000 calories.

The same £1 employed in purchasing electric energy at the cheapest rate (Class I., water) yields one electrical horse-power for 5,840 hours, and is therefore equivalent to 3,764,136,960 calories. This is just about one-quarter of the yield from direct combustion of an equivalent value of coal.

It may be assumed that the labour and wear and tear of the furnace will, taken together, be about equal in each case.

The heat produced electrically can, however, be much more usefully employed, so that a true comparison of the cost of heating processes by the two methods can only be made in the full light of experimental data determining the efficiency of each furnace or apparatus.

When it is remembered that the efficiency of many non-electric furnaces is barely 10 per cent. of the theoretical and very few will exceed 25 per cent., whilst the efficiency of electric appliances sometimes reaches 75 per cent. and is often 50 per cent., it will be seen how closely this cheap power of to-day is competing with fuel combustion, even as a mere source of heat for metallurgical or chemical reductions.

In the case of different water-powers a great deal of variability exists as to the possibilities of economy. The cost of labour and upkeep for a modern generating plant, actuated by water-power, with good machinery and untroubled by any irregularities of working may be easily reduced to a perfectly nominal sum (about 4s. per horse-power-year is sufficient in such cases for any fair-sized plant, and with very large plants it may be brought down to half that sum). The gross cost of the power to the consumer then becomes practically dependent on the amount of capital charges (and valuable private rights) involved. These items will vary enormously according to

ment in every possible way by short-sighted anti-foreign legislation aimed especially at the exclusion of foreign capital—a policy which (like most selfish policies in the sphere of world-politics) a more advanced order of intelligence would see hurts far more the nation adopting it than it can ever hurt the foreign capitalist who has other fields for his energies to choose from if he is excluded from this one. It is my opinion, after studying this question a good deal from all sides, that short of carrying the waterfalls themselves out of the country (which, of course, is impossible), there is no possible way in which the free admission of foreign capital can do anything else than benefit Norway.

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whether the flow of water is naturally even all the year round, or whether expensive dams must be constructed to regulate it, whether the pipe is long or short, the fall high or low, whether much valuable property is submerged by damming, and other conditions.

By designating the various water-powers Class I. and Class II., I distinguish in a rough, practical way between those powers where a high cost of regulation or of development has been necessary to bring the water to the place of consumption and to insure an even supply all the year round, on the one hand (Class II.), and those cases where these essential objects have been provided more or less completely by natural conditions (Class I.), thus rendering the total capital employed much lower.

In general it may be stated that a capital expenditure of £7 os. od. per e.h.p. capacity is sufficient for the development of powers of Class I., including all necessaries up to the dynamo terminals; whilst some few powers which exist in Western Norway can be developed still more cheaply. On the other hand, water-powers have been developed in England and in other countries which have cost upwards of £60 os. od. per electrical horse-power for harnessing equipment and compensations. The total equipment at Niagara Falls cannot have cost less than £30 os. od. per horse-power in spite of the very large scale of operations.

It is needless to say that unless it be undertaken for some very good and exceptional reason such an expenditure as £60 per horse-power in the light of our modern understanding of this subject is quite prohibitive and ought not to be seriously proposed.

In considering the various water-powers available throughout the world there are, of course, many intermediate stages between these two extremes, and in some of these stages it may be possible to set some royalty value on the water rights. In general, however, it may be assumed that only powers which are strictly of Class I. will be able to successfully demand royalty values, and that powers of Class II. (and intermediate stages) will only be developed in future when some public object is to be served by their employment.

The grants for such powers will mostly be free, or nominal royalties only will be charged.

The powers of Class I. (especially the best ones) are not very numerous, and their enormous natural advantages will to some extent be neutralised by the high prices which will naturally be placed on the water rights by owners, when their true values become known and when a ready market is opened for them. Nevertheless, I believe it is almost exclusively to powers of this type that we must look for the future of such gigantic possible developments as are suggested to-day by the looming processes of electrolytic iron, nitrate production, and the complete treatment of complex sulphide ores—three fields of enterprise, any one of which, if successfully developed, must rapidly exceed in magnitude the entire industry of electrometallurgy as it exists to-day.

As this class of water-power seems destined to play so important a *rôle* in the near future, it will be of special interest here to give a concrete instance of such a water property and the method employed in Norway for arriving at the capitalised value of the water-right. The example is drawn from one of the most favourably situated of the many favourably placed of the small powers in western Norway, where the existence of these sources of energy on the verge of deep water and ice-free harbours suitable for any kind of shipping, is probably unique, offering advantages to industry found nowhere else in the world in such happy combinations.

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The property was acquired about eight years ago from the former Norwegian owner. The purchaser left some mortgages standing, so that the capital stood as noted below when he succeeded in obtaining title (a royal concession under the Foreigners' Exclusion Acts) to own the property. Extensive surveys had been made, the statistics of rainfall, &c., obtained, and the engineers had pronounced the waterfall (which had a fall of 1,000 feet, with a very short distance for tunnel and for pipe line from the outlet of the last lake to the lowest level) to be good for about 7,500 kw. (10,000 e.h.p.), and capable of development for less than £5 (kr. 90) per h.-p., which sum was to include also some payments to farmers for fullest damming rights. It also included the cost of damming the principal lakes at a very favourable spot, whereby, for the comparatively small sum of £5,000, enough water could be stored in the large lakes to completely equalise the fall all the year round, and so use nearly every drop of water that falls on the watershed. Though the total area of the watershed was small, viz., about 40 square kilometres, the annual rainfall is the highest in Norway, reaching 3,600 mm. per year. There was therefore enough water to secure 3·8 cub. m. per second all the year round after liberal deductions for evaporation and loss. The lake basin was large enough to secure complete equalisation of the supply. Also the intervals of drought are never very protracted when compared with such periods in countries like England. All these circumstances are most favourable for cheapest development.

TABLE II.

SHOWING INFLUENCE OF THE COST OF DEVELOPING A SMALL WATERFALL (AND INSTALLING MACHINERY) ON THE CAPITALISED VALUE OF THE WATER RIGHT AND FREEHOLD. SHOWING ALSO METHOD OF CALCULATING RETURN ON CAPITAL INVESTED.

The fall has a capacity of ca. 7,500 kw. It is supposed that a contract (with suitable guarantees) has been obtained for renting 6,000 kw. at an inclusive charge of £2 10s. per kw. delivered at switchboard (= £1 17s. 6d. per e.h.p.).

According to latest estimates and all existing contracts the expenditure required will be as follows, viz. :—

	£	s.	d.	£	s.	d.
Earthworks—						
Tunnel 300 m. long @ £4 8s. 3d. ...	1,323	5	0			
Intake, masonry, &c.	555	0	0			
Pipe track levelling...	555	0	0			
Dam at Rörvik lake and cuts	5,555	0	0			
				7,988	5	0
(N.B., equal to £1 6s. 6d. per kw.)						
Buildings—						
One power station, two valve houses, sundry observation boxes, telephone posts, and sluiceman's house				2,666	0	0
(N.B., equal to 9s. per kw.)						
Ironworks—						
One pipe line of 800 m. length with all sundries	6,222	0	0			
Sluices for dam, intake, and cuts... ...	555	0	0			
				6,777	0	0
(N.B., equal to £1 2s. 6d. per kw.)						

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Machinery—						
Pelton wheel turbines, dynamos, and regulators	12,777	0	0			
Transformers and 2-kilo line	7,222	0	0			
Electrical outfit	1,110	0	0			
				21,109	0	0
(N.B., equal to £3 10s. per kw.)						
Special Charges and Allowances—						
Extra compensation to farmers, payable on exercise of damming rights as per contracts	2,220	0	0			
Special tax demanded by Herredsstyrer	1,387	0	0			
Contingencies on building estimates ...	2,277	0	0			
				5,884	0	0
(N.B., equal, say, to £1 per kw.)						
Total development cost as estimated ...	44,424	5	0			
General margin for contingencies ...	5,555	0	0			
				49,979	5	0

This expenditure can be provided for by the issue of £33,333 preference shares and £16,665 by bank loan on mortgage or debentures. The water right can be paid for by the issue of £50,000 in ordinary or deferred shares.

The complete scheme of capitalisation will then be as follows :—

	£	s.	d.	£	s.	d.
Existing mortgages	13,888	0	0			
Bank loans	16,665	0	0			
Preference shares, 8 per cent.	33,330	0	0			
Ordinary shares to owners of water rights	50,000	0	0			
				113,883	0	0

The apportionment of revenue will be as follows :—

Working Expenses—						
Wages, materials, taxes, and administration...	1,665	0	0			
Amortisation of plant and renewals—						
Buildings, 10 per cent. on £2,665 ...	267	0	0			
Ironworks, 5 per cent. on £13,000 ...	650	0	0			
Machinery, 5 per cent. on £13,888 ...	694	0	0			
Earthworks, 2½ per cent. on £8,000	200	0	0			
				3,476	0	0
Capital Charges.						
Mortgages—						
Interest at 5 per cent. on £13,888 ...	694	0	0			
Redemption fund 10 per cent. on £5,555	555	0	0			
2½ per cent. on £8,332	208	0	0			
				1,457	0	0
Bank loan—						
Interest 6 per cent. on £16,665	1,000	0	0			
Redemption fund 5 per cent. on... ...	833	0	0			
				1,833	0	0
The share capital—						
Preference shares £33,330 at 8 per cent.	2,666	0	0			
Ordinary shares £50,000 at 8 per cent. ...	4,000	0	0			
				6,666	0	0
				13,432	0	0

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Revenue—			
6,000 kw. sold at £2 10s. per kw.	15,000	0	0
Margin +	1,568	0	0

This fall costs only £7 8s. per kw. to develop and equip. It is therefore possible to place a considerable value on the water-rights.

If the same revenue is obtained from another waterfall (B) which, owing to less favourable natural conditions, will cost £8 5s. per kw. to develop and equip (an average cost in Western Norway), or from a third fall (C) costing £11 2s. per kw., then, omitting the ordinary shares altogether in the case of (C), and valuing the water-right at £25,000 in ordinary shares in the case of (B), the account will stand as follows :—

	B. £	s.	d.	C. £	s.	d.
Total cost of development with margin in same proportion as before	58,333	0	0	77,777	0	0
Schemes of Capitalisation—						
Existing mortgages before for the sake of comparison	13,888	0	0	13,888	0	0
Bank loans	22,220	0	0	27,775	0	0
Preference shares 8 per cent. ...	36,105	0	0	49,995	0	0
Ordinary shares for water right ...	25,000	0	0	—		
Total capitalisation	99,213	0	0	91,658	0	0
Apportionment of revenue as follows :—						
Working Expenses—						
Wages, materials, taxes, and administration as before	1,665	0	0	1,665	0	0
Amortisation of plant...	2,316	0	0	3,088	0	0
Capital Charges—						
Mortgages as before	1,488	0	0	1,458	0	0
Bank loans, 6 per cent. and 5 per cent.	2,444	0	0	3,055	0	0
Preference shares, 8 per cent. ...	2,888	0	4	4,000	0	0
Ordinary shares, 8 per cent.... ...	2,000	0	0	—		
	12,771	0	0	13,266	0	0
Revenue as before	15,000	0	0	15,000	0	0
Margin	2,229	0	0	*1,734	0	0

The £50,000 ordinary shares in the case of Fall (A), and the £25,000 ordinary shares in the case of (B), and nothing (by comparison) in the case of (C), therefore represents the fair valuation of the water right, and when it is considered that the returns on these deferred shares rank after the preference shares and mortgages, and the revenue will gradually rise to 12 per cent. on all shares during the currency of the long contract by reason of the accumulation of the sinking funds for extinction of the loans, it must be allowed that the valuation is not excessive.

There have been cases in Norway where the price of electric energy is said to be still lower than the figure I have selected as a probable minimum,

* Without any dividend for ordinary shares.

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viz., £2 10s. per kw.; for instance, at Meraker, near Trondhjem, the power 3,000 h.p. has been sold at £1 5s. 6d. per h.-p. on a seven years' contract, and at Notodden I believe the price was £1 8s. for 3,000 e.h.p. It is not easy, in the absence of exact statements such as I have given above showing what allowances are set aside for interest on capital, sinking fund, &c., in stating such prices to make a comparison with the figures I have stated from my own experience. It may well be that when such investments become more popular lower returns on capital will be accepted, in which case the sale price may become proportionally lower without reducing the value of the water-right. For example, if for the development of the above-quoted waterfall supplies of capital could be obtained at a uniform rate of 5 per cent. (including interest and sinking funds), then, leaving all other items of expense the same (including depreciation on the works and plant), the price of the energy might be reduced to £2 per kw. and the value of the water-right remain as above stated.

It is by no means certain that there exist a very large number of powers which can be developed at even so low a cost as to permit of the sale of the energy at £2 per e.h.p. year (£2 10s. per kw. year) either in Norway or anywhere else; the value of such water rights may therefore very likely rise much above the value indicated by these estimates. For instance, if the current price of energy in the next few years finds a level at £3 per kw. year, the capitalised value of the undeveloped fall (A) in question would be about twice that shown in the table.

It may be added that although the above valuation is self-evidently a just one, yet so little attention has been drawn to those remarkably favourable opportunities of producing cheap electrical energy with low capital expenditure and low working costs and under highly favourable conditions for its utilisation, that such values as those indicated by the above figures are not always attached to these properties as yet. How long this opportunity of reaping a large increment on capital combined with intelligence will remain open is a matter for the intelligent foreign capitalist and the Norwegian Government to decide between them.

My belief that this subject has not received nearly enough attention, and that its great importance to the early expansion of electrolytic and electro-thermal industries, which it is this Society's special mission to foster, has been somewhat overlooked, must be my excuse, if excuse is needed, for this special advocacy of a single class of motive power and for the simple nature and the purely commercial treatment of the subject chosen for this paper.

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REVIEWS OF BOOKS.

Stoichiometry. By SIDNEY YOUNG, D.Sc., F.R.S. (Textbooks of Physical Chemistry). Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S. (London: 1908. Pp. lxi. + 381. Price 10s. Longmans, Green & Co).

This book commences with an Introduction to the Study of Physical Chemistry by Sir William Ramsay, which takes up 50 pages. This Introduction has already appeared and can be obtained separately, consequently it is not necessary to review it here.

The book begins with a discussion of the Fundamental Laws of Chemical Combination, the first portion being more or less historical. Under the definition of an element the author remarks that from time to time it has been suggested that bodies now classed as elements have, in the first place, been formed by the condensation of one or a few primary forms of matter—in other words, that the elements are either polymers or a very stable form of compound. It has been practically proved that radium emanations gradually become degradated into helium, and if radium is taken as an element, then it must either be a polymer of helium or else a compound of helium with some other yet undiscovered element. Of course, the idea that elements are built up from one primordial substance is not new. It will be strange if increased knowledge finally shows that the conception of the older chemists was more accurate than the theories of those who follow them.

The chapter goes on through the Law of Definite Proportions to the Atomic Theory, which, to our minds, is written in an unnecessarily abbreviated form.

The next chapter deals with the general properties of gases and then follows the determination of atomic weights. The author lays stress upon the experimental errors which, even when the greatest care is employed, almost invariably occur, and he remarks that no observer, however expert, can hope to obtain absolute accuracy in any measurement, however simple. Consequently one has to work in such a way that a large number of determinations are made and the arithmetical mean of the individual values is taken as the final result. Before anyone who has not already taken up the study of atomic weight determinations commences work of this kind he would be well advised to read this section.

The next chapter deals with the periodic system of the elements, tables and diagrams being given to show the various relationships of the elements to each other. Thus there is one table which is not usually come across in textbooks on chemistry—the table of hydrides and halides, and the electrochemical character of the elements is also indicated by another table. The properties of liquids are dealt with very fully and also the kinetic theory of gases, the properties of solids, and the properties of dilute solutions. The freezing-point and boiling-point methods for determining the molecular weights are fully gone into, and the last part of the chapter deals with Osmotic Pressure.

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In the last chapter the determination of molecular weights from chemical considerations is considered, the different methods by which the determinations are carried out being given.

This book is a very useful addition to the series of textbooks of physical chemistry, and the author is to be congratulated upon the care which he has taken in compiling the matter and the success which has rewarded his efforts.

Sir William Ramsay's object in editing this series of books is to cover the whole field of physical chemistry thoroughly, and his hope is that by bringing the books out in the form of volumes under different headings and by different authors, instead of making one complete book, the final result will be less cumbersome, more thorough, and the subjects may be kept more up to date. Whether this is altogether an advantage to the average student who has an enormous amount of work to digest it is difficult to say. That it is of very great value to have such memoirs there is no doubt, but there is a tendency sometimes for disconnection, and may there not be a fear on the part of the authors that they are treading upon ground covered or to be covered by some one who is writing a different volume of the series? As a rule we have not noticed this to any great extent, but it must be admitted that occasionally this tendency is noticeable.

The Construction and Working of Large Gas Engines. By P. R. ALLEN.

This small octavo volume of 120 pages and 7 plates is the reprint of a paper read before the Manchester Association of Engineers on January 11, 1908, and it would have been better if the author had given this information on the title-page instead of burying it in an obscure part of the book where it can only be found after prolonged search. The reprint suffers also from the absence of any division into chapters and from the lack of an index.

Having made these criticisms on the form in which the author has published his monograph, the writer can now devote himself to commendatory remarks. The contents of the book are described with exactness in the title, and the author has dealt in a most practical manner with details of the construction and working of large gas engines—that is, of engines of more than 500 h.p.

The arrangement and size of cylinders for large powers on the Otto Körting and Oechelhauser systems, flywheels, stuffing-boxes, ignition apparatus, lubrication, starting the engine, silencers and exhaust heat apparatus, and gas-engine troubles are all dealt with, in considerable detail.

An appendix gives details of the cost of power by steam and gas and also a tabulated statement of the dimensions of the principal parts of a 750-h.p. engine by various makers.

The following paragraphs give the author's views on the future of the large gas engine :—

"The small gas engine occupies a sphere of usefulness of its own ; it is generally relatively economical compared with other motors and requires but little attention, but its strong point is its convenience. The large gas engine has to justify its existence under much more onerous conditions, and in meeting the large steam engine has to compete with a machine which has had more than a century of close attention from the most able engineers of the day. Although the large gas engine has developed in a phenomenal way during the past ten years, much remains to be investigated on the theoretical side, while no finality has yet been reached from the point of view of the builder ; but even in its present condition the large gas engine has attained a sufficient degree of perfection to recommend itself not only to the

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manufacturer who wishes to cut his coal bill in half, but to the political economist on the broader ground that any prime mover which will tend to prolong the life of our chief national asset—the British coalfields—is a machine which will be of great assistance to the State."

It only remains to be added that the book is well printed, that the illustrations are good, and that it is well worth a place in the technical library of all interested, either as makers or users, in the modern gas engine.

Monographien über angewandte Elektrochemie. Vol. XXX. **Thermoelemente and Thermosäulen.** By Dr. FRANZ PETERS. (Halle: Wilhelm Knapp, 1908. Pp. vi. + 184.)

Thermo-elements are now so largely employed in electro-chemical and chemical industries that the introduction of a book upon the subject is a valuable addition to the Monographs on Applied Chemistry. The fact that two dissimilar metals when joined together will give an electrical current when heated at the junction was shown so far back as 1801 by Ritter. Seebeck in 1821 showed that when a copper plate and a rod of bismuth were soldered together on heating the junction a current was produced which caused a movement of a magnetic needle.

The action of heat upon metals when joined together has been employed—

I. To form a thermo-battery from which electrical energy can be obtained.

II. As a means of measuring temperature, particularly high ones where an ordinary thermometer cannot very well be employed.

Dr. Peters first describes the thermo-batteries. The first chapter deals with the history of thermo-electricity. In the next section the construction of the thermo-batteries is treated of. It is shown how different metals and different combinations of metals and alloys can be used, and it is likewise explained which are the most satisfactory and which form of apparatus gives the best result. Although this part of the book is very interesting and is ably written, we are inclined to think that the final part, dealing with the employment of thermo-elements for measuring temperatures, is the more valuable.

Pyrometers were at one time very expensive because almost the only metals employed in their construction were of the platinum group—for example, platinum and an alloy of Rhodium-platinum or platinum iridium. Now, however, that cheaper alloys have been found to act satisfactorily—for example, those used in the Bristol pyrometer—this form of measuring instrument is being very widely employed.

This book is a most useful addition to the already valuable series of volumes upon applied electro-chemistry. It is well illustrated, and the author has evidently been at great pains to make it a complete survey of the subject.

Monographien über chemisch-technische Fabrikations Methoden. Vol. XI. **Der Dampf in der chemischen Technik.** By W. MOMBER. (Halle: Wilhelm Knapp, 1908. Price M. 3, P. 60.)

The importance of steam in chemical manufacturing processes cannot readily be over-rated, and it is therefore a very good idea on the part of the publishers of these technical monographs to issue a volume dealing with this subject.

The book before us commences with a note upon the various purposes for which steam is employed. The author then refers to the physical nature of

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steam, partly in rather an elementary manner and partly in a more advanced way. He then treats of fuel and gives a table showing the number of calories given off by various fuels, such as ordinary coal, peat, wood, petroleum, producer gas, and so on.

The various forms of boilers are then described, and we notice—and perhaps it is to be expected—that the German plant are described in greater detail than those of other countries. It is mainly in connection with boilers, such as are used for steam engines, that this part of the book is written.

The next section treats of steam turbines, a subject which one would hardly have expected to have met with in a volume of this title. But a moment's consideration shows that this is not really out of place, because, of course for power purposes, steam turbines are now coming into very general use. The various evaporating plant are then dealt with, and heating with steam under pressure such as autoclave work. Methods of evaporation, of rectification, and distillation in currents of steam also find a place in this monograph. This will certainly be found very useful, but it would have been much more valuable if the author had supplied an index.

Canada : Department of Mines—Summary Report of the Mines Branch, 1907-8. (Ottawa : 1908. Pp. 100. Price 10 cents.)

The Report, which is of considerable general interest, includes a short account of recent progress in Electric Smelting. Among lately-invented systems the Lash process for the direct production of steel, which is being tried at Niagara Falls, is described. The typical Lash charge consists of 54 per cent. iron ore, 27 per cent. cast-iron borings or granulated pig-iron, 4 per cent. sawdust (to make the mixture porous), 4 per cent. limestone, 3 per cent. coal-tar, and 8 per cent. coke. Successful results have been obtained, it is claimed, heating this mixture direct in the electric furnace.

The Electro-Metal Company (Ltd.) are building a 500-h.p. Héroult furnace at Welland, Ont., and if this is successful larger furnaces will be immediately built.

At Nelson, British Columbia, a Snyder induction furnace for the production of lead bullion and spelter in one operation has been erected, power being supplied by the Bonnington Falls. The Report includes an Appendix by Mr. A. Grönwall on a comparison of the various induction furnaces (Kjellin, Frick, Röchling, and Electro-Metal Co.) at present in use. *Apropos* of induction furnaces, reference is made in the Report to the observation of Dr. A. Schmidt that the desulphurisation in the Kjellin furnace is to be ascribed to the iron oxides added and to the specific influence of the alternating current, which produces, it is stated, molecular oscillations in the bath, rendering more active the combination of the sulphur in the bath and the oxygen of the added ore.

Laboratoriumsbücher für die chemische und verwandte Industrien. Vol. III. Laboratoriumsbuch für die Industrie der Riechstoffe. By Dr. Oskar Simon. (Halle : Wilhelm Knapp, 1908. Pp. vi+67. Price 3 marks.)

This little monograph will be found very valuable in the laboratory, for which, of course, it has primarily been written. It commences with a general description of the methods employed in the examination of ethereal oils and perfumes. The section is divided up under the different headings : Physical Methods, Chemical Methods, Examination of some Ethereal Oils,

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Identification of some of the chief adulterants which are found in Ethereal Oils.

The second part deals with the particular methods employed, and a short notice upon the most important perfumes. The sub-divisions of this part are: Ethereal Oils, Natural and Synthetical Chemical Individuals, Balsams and Resins, Animal Raw Products. The descriptions of the various individual products given and the physical constants will be found very useful for purposes of identification, and we congratulate the author upon his work.

The National Physical Laboratory: Report for the Year 1907.

There is much among this record of splendid work accomplished or promised that is of special interest to the electrochemist. In the Physics Department work on the silver voltameter and the electrochemical equivalent of silver has been carried on by Mr. F. E. Smith, in conjunction with Mr. T. Mather, F.R.S., and Dr. T. M. Lowry. It is concluded that an easily reproducible voltameter can be specified, and in this form the passage of a coulomb of electricity always causes the deposit of a definite mass of silver, and that therefore the ampere can be defined accurately to 1 part in 100,000. It is interesting to note in this connection that the ampere (and not the volt) was chosen as the second primary standard at the recent International Conference. This work is being continued during the present year, especially with a view of elucidating the differences in the results obtained by other observers.

In the same Department work on the Weston cadmium cell has been continued, and it is concluded that this standard cell can be set up by different people with different materials and still have E.M.F.'s agreeing to a few parts in 100,000.

In the Photometric Department the reproduction of the Violle standard of melted platinum is in contemplation, and in view of this the valuable work of Dr. Harker, who is constructing large electric refractory-oxide tube furnaces of the cascade type, will prove of special importance. This brings us to the Thermometric Department, where Mr. W. A. Price has been improving carbon tube furnaces, and has evolved a form capable of heating uniformly fairly large objects up to 2,500° C. In this the melting and boiling points of a number of refractory substances are being studied, and this work is now being continued in the new fire-proof room specially erected for the purpose of high-temperature research. This will include investigations into the properties of fused silica ware and the strengths of other materials at high temperatures and a special electric furnace with automatic photographic temperature recorder has been installed for the purpose. Other high-temperature work is being carried out in the Moissan arc furnace and the Gröndel-Kjellin furnace, in which the behaviour of metals and alloys can be studied in the absence of flame gases.

The Metallurgical Department is now the permanent home of the investigations undertaken by the Alloys Research Committee of the Institution of Mechanical Engineers, whose work last year was concerned with the alloys of copper and aluminium, and of certain ternary alloys of aluminium. The latter investigations are being carried on, as are also the eutectic alloys researches of Mr. Rosenhain and Mr. Tucker. In the new building for metallurgical chemistry, which is now open, a modified form of Dr. Sand's apparatus for the rapid electrolytic determination and separation of metals has been installed.

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Introduction to Metallography. By Dr. PAUL GOERENS. Translated by FRED IBBOTSON, B.Sc., A.R.C.Sc.I. (London, 1908: Longmans, Green & Co., 39, Paternoster Row, E.C. Pp. 214. Price 7s. 6d. net.)

This is an admirably clear exposition of the physico-chemical principles underlying the study of the minute structure of metals, the statement of general theory and its application to particular cases leaving little to be desired in the way of lucidity. An introductory chapter on Cooling Curves and their determination leads up to a discussion, first of Aqueous Solutions, then of Solid Solutions (fused salts), and finally of Alloys. This last chapter covers a very wide field, dealing, in brief, with practically all the binary and ternary combinations that have been studied up to the present. A useful chapter on the Practical Microscopy of Metals and a final chapter, well illustrated, on the Metallography of Iron and its Alloys complete the volume.

The book contains a few faults of style incidental, perhaps, to the translation, and some omissions due to the English version (except the last chapter) not having been brought quite up to date, but apart from this it will make an excellent text-book for men beginning the study of a difficult subject, which it tackles in a clear, interesting, and practical manner.

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Transactions
OF
The Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. IV. APRIL, 1909. PART 3.

THE INFLUENCE OF CHEAP ELECTRICITY ON ELECTROLYTIC AND ELECTROTHERMAL INDUSTRIES.

BY E. A. ASHCROFT, A.M.I.C.E., M.I.E.E., &c.*

(*A Paper read before the Faraday Society, Monday, December 21, 1908, DR. N. T. M. WILSMORE in the Chair.*)

DISCUSSION.

Mr. W. R. Cooper (*communicated*) : There is no doubt, of course, that cheap power is the essence of success in certain electrochemical industries, namely, wherever the cost of power is a considerable portion of the whole.

There is always a difficulty when discussing the cost of water-power, for the simple reason that the cost of such power must depend upon the price that it will fetch, and this price is not likely to have any fixed value. In dealing with coal, we know that the price of coal cannot vary beyond certain limits, but if a contract is made for water-power for, say, seven years, it does not follow that the price of the water-power subsequently will not be raised, owing to the greater demand for power in that particular neighbourhood.

I do not suppose there is any doubt that the price of water-power will tend to go up considerably; but, on the other hand, the cost of power from various kinds of fuel is likely to go down, though possibly not to a very serious extent. It follows, therefore, that water-power should be purchased outright by the companies running electrolytic or electrothermal industries, and not merely leased.

Mr. Bertram Blount thought the author had been a little hard on sources of power other than water. In many electrochemical industries questions of freight, labour, &c., gave the advantage to more costly sources. The notion frequently held that nothing but the cheapest power, say, 30s. per kw. year, was of any use to electrochemical methods was erroneous. It was a strange but undoubted fact that however costly electric heating appeared to be, its economy in application frequently counterbalanced its

* This Paper was published in the volume of *Transactions* (vol. iv., part 2, p. 134) issued in October, 1908.

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high prime cost. It was for this reason that he believed there was a great future for processes such as electric zinc-smelting, although up to the present so little had been achieved commercially in this direction.

The 13s. per kw. year allowed by the author for capital charges in the case of the best water-powers (p. 135) seemed to him high, but, of course, the shortsighted policy of impeding industry pursued by the Norwegian Government had to be borne in mind.

The Paper was based on calculations of cost of power to be made and sold as such, but a different point of view might be adopted, according to which the power was produced by the consumer. This was certainly a more favourable state of affairs.

Mr. W. Murray Morrison agreed with the author that the subject had not received sufficient attention, and he was glad that it had been brought before the Society for discussion. He took it, though it was not stated in the Paper, that in all cases the author's figures were based upon a load factor of 100 per cent., and he thought Mr. Blount was right in his criticism of the author's treatment of steam and gas engines. The cost of £8 6s. 6d. per kw. year given for electric energy generated by the former was high, and he thought that under favourable conditions electricity could be produced from steam for probably as low as £5 per kw. year. In the case of gas engines, also, he knew of cases where very good results had been obtained on a large scale, especially where valuable by-products were produced. He thought, however, that the author's charges for labour were considerably understated in both these cases. It might very possibly be the case that the capital cost, and hence interest charges, in the case of steam and gas plants were less than those for a water-power plant of an equivalent size, but the depreciation charges would be much greater, as also labour and stores, and the fuel costs would be an extra.

He did not altogether agree with Mr. Ashcroft in his classifications of water-powers. His Class I. was a very good example of a fall, but one not often met with, and certainly not on a large scale conveniently situated. His Class II., however, was a bad specimen, and there were many intermediate in value between the two classes. The author had unduly penalised Class II. as far as labour and upkeep were concerned. There would be greater depreciation in the case of cheap powers, where the capital would be mostly sunk in plant, than in dearer powers, where the money would be chiefly spent in earthworks, &c., and in royalties. Again, the £4 2s. per kw. year capital charge in the case of Class II. meant that about £40 per kw. must be spent on plant, &c. This was an exorbitant figure. It was these considerations that made him think that the differences between Classes I. and II. stated in the Paper were excessive. The English plant quoted by the author (p. 138), on which £60 per h.p. had been spent in capital expenditure, must have been a very small one, as the price was one which no engineer or capitalist would care to consider.

Referring now to Table II., he noted that the cost of construction amounted to £7 8s., contingencies to 18s., and purchase consideration (*i.e.*, existing mortgages and payment in shares) to £10 14s. per kw. installed. This gave a grand total of £19 per kw.—by no means a low figure. Even these figures, however, were based largely on estimates, and without great experience at the back of estimates of this kind they usually fell short of what was required. He certainly thought the author had allowed too low a figure for the plant, and had not left sufficient margin for contingencies.

He himself had been pretty well all over Norway, and he had many "raw" properties (that is to say, land and undeveloped water-rights) offered

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him at prices equivalent to about 10s. per kw. If Class I. powers were brought down to this figure, they would be more attractive, but he feared not many such were to be found.

There were one or two other considerations worth drawing attention to. The position of the source of capital and of the management was of some importance in connection with labour questions. Foreign capital usually carried with it its own labour, and unless this was done on a very large scale labour troubles were pretty sure to arise. This was a contingency worth bearing in mind. Added to the safeguarding of capital, management, and labour, numerous other considerations called for careful investigation before fixing on the site of a power supply, such as source of raw materials, market for finished product, freights, possible tariffs, or other restrictions. While agreeing with the author that well-chosen and well-designed water-powers opened the way for the successful operation of many electrometallurgical and electrochemical industries, in a manner which no other source of energy was likely to do, he did not go so far as the author in saying, as he did, that such alternative sources of energy had in all cases "no chance at all," or that water-powers strictly of Class I. were the only ones to be looked to for the attaining of the desired and necessary economy.

He quite agreed with the author in thinking that no two water-power schemes were alike, and each should be considered on its merits. Generalisations in this connection were therefore to be accepted with great caution, for conclusions reached for a particular water-power scheme, as well as for a particular industry and a particular country, could not be applied elsewhere without taking every possible difference of conditions into consideration.

Mr. Charles Weiss said he had taken especial interest in the available water-powers in Bavaria and the Bavarian Highlands. Apart from private owners of water-rights, the swift-flowing rivers and several lakes belonged to the State, and the latter had introduced legislation retaining State control of their water-rights, and only leasing them to manufacturers on conditions beneficial to the State. But it was proposed to use the electrical energy generated first for the shorter State Railway lines in South Bavaria. Some people in England might call this socialistic legislation, but in Germany the State took much greater powers for the benefit of the people.

He agreed with previous speakers who had dwelt on the existence of cheaper steam-produced electrical energy than was allowed by the author; and he knew of at least one case in this country where electricity in bulk for a 100 per cent. load factor could be had at under £6 per kw. year from steam turbo-generators. For certain electrochemical industries this price was quite acceptable.

Mr. Leon Gaster: I fully appreciate the importance of employing waterfalls, &c., for the generation of electric power for electrochemical purposes, and so preserving our diminishing stores of coal; as water-power, unlike coal consumption, involves no actual using up of valuable and unreplaceable material, this course is obviously desirable.

However, the feasibility of the system is often influenced by other factors, such as transport facilities, supply of material, and labour, besides the actual economy of power conversion. The nature of the water supply, &c., as the lecturer pointed out, may render the original cost of installation very heavy, and this may be accentuated by ill-advised and even prohibitive legislation. In Norway, where the conditions are specially favourable for the development of water-power, the legislation ought to be much modified in order to stimulate the investment in the country of foreign capital.

Inconvenient legislation is also sometimes resorted to on æsthetic grounds.

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For instance, I was informed that at Niagara an agitation against destroying the natural beauties of the falls (originated, it is believed, by parties interested in coal in the United States) resulted in legislation restricting the use of the water to but a fraction of that originally contemplated. Naturally, therefore, the first cost of the installation now appears needlessly high for the present output.

With the increased utilisation of water-power manufacturers have greatly improved the design of turbines, which are now suited to both high and low falls, and answer all requirements. The matter is also engaging the attention of many Governments whose representatives are undertaking a survey of the available sources of power, with the view of framing legislation for their ultimate extensive use. Gas engines and steam turbines can now be constructed with higher efficiencies than those mentioned by the author. I should, therefore, like to know what was the size of the plant which the author had in view in compiling the comparative costs shown in Table I. on page 135. With cheap water-power as described by the author it may be possible to economically establish many lucrative electrochemical manufactures in Europe which are now developed in the United States of America.

Dr. H. Borns remarked that the author had not drawn attention to some of the disadvantages of water-powers, such as the troubles due to occasional dearth of water and to ice. Was there no need of a steam-power reserve?

Mr. E. A. Ashcroft: Ice difficulties do not exist in Norway, where water can usually be drawn off many feet below the surface of the supply, although they do exist in Sweden and Finland.

Dr. H. Borns: This must give Norway a great advantage.

Professor R. H. Smith said the ice question referred to by the last speaker was an important one, for although W. Norway appeared to be particularly favoured in this respect, most localities were not so. He had in mind the power plant at Valtellina in the Alps for supplying the railway with current, where the exclusion of ice from the channels cost considerable money and trouble in the design of the works.

The enormous variations in supply during the year and the consequent expense of provision therefor was another point which told against water-powers.

He assumed that the figures in Table I. were calculated on a load-factor basis of 100 or full load for 8,760 hours per year. Of course under those conditions it was easy to get good results. On that basis of 8,760 hours full load per year his figure of £6 9s. 6d. for steam engines worked out to 0·18 of a penny per h.p. hour. On the same basis his (Prof. Smith's) calculations in the chapter on "Capital and Working Costs" of his book upon "Commercial Economy of Steam and other Heat Engines" would give practically the same result for condensing engines; but the figures given in that chapter were worked out for $50 \times 54 = 2{,}700$ hours full-load working per year. The cost varied greatly with the class of steam engine, gas engine, or oil engine, and on the size of the installation, as also, of course, with the price of fuel. These variations were fully illustrated on pages 129 and 137 of the above book. He did not see how it was possible even with water-power to reach the low figure of £2 per kw.-year, and certainly not in Great Britain.

In the figures given on page 140 of the Paper the author allowed 10 per cent. upkeep for buildings and only 5 per cent. for machinery. This relationship was surely extravagant. Did he rightly understand these allowances to be for upkeep only, seeing that depreciation was not specially mentioned? In his opinion the importance of depreciation was not fully recognised in England, and the result was that electric power was frequently being sold here for under cost price. This was being done in the case of the

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older electric lighting stations which were built for lighting only and could not compete with the modern stations. In order to fill up partially the valleys in their lighting load curves, they sold current for power without debiting this power supply with any reasonable proportion, sometimes with no share at all, of capital charges. Chemical engineers would be wise to reckon on the impossibility of electric power being produced in this country for less than 1d. per unit delivered to the consumers.

Dr. E. Feilmann said that the success which had lately attended the production of gaseous fuel from peat had very favourably influenced the cost of power from gas engines ; large installations for gasifying peat by the well-known Mond process were now either at work or in construction in England, Germany, and Italy, that in the latter country being designed for a production of 3,000 i.h.p. The ammonium sulphate produced as a by-product was stated to bring down the cost of the gas to almost zero, and in some cases it was said that it even paid to burn it to waste. Under such conditions the cost of power from a gas engine must approach very nearly to that from the author's Class II. waterfall.

He did not believe that the electric smelting of iron could be carried out on a commercial scale for many years to come. According to Härdén (*Elect. and Met. Ind.* 7. 16) we had an expenditure per ton of iron in electric smelting of $4·80 in fuel for reduction, $3·90 for electric power, and $1 for electrodes ; this was on the assumption that power costs $20 per kw. year, but even at half that price, or £2 10s. per kw. year, the cost was $7·75 per ton for electric smelting, as against $6·84 per ton for smelting in the blast furnace, according to Härdén's figures, which omitted the cost of labour, which was estimated to be about the same in the two cases.

Mr. E. A. Ashcroft, in reply, said he was glad the Paper had given rise to so interesting a discussion.

As regarded the criticisms that had been made, he thought these, in many cases, had answered one another. The special object of the Paper seemed not to have been made perfectly clear. He was not advocating water-powers as against steam or gas *per se;* that was a much larger question, and had been pretty thoroughly discussed and written about in other places. He was merely trying to call attention by this Paper to the very special kinds of water-power that still existed in a few favoured localities, but were somewhat rare, and which, if developed, would allow electrochemical industries to grow up that otherwise could not exist. It seemed to him a matter of great importance to call general attention to the existence of economical conditions in the Norwegian Falls which will in the future render practicable electrolytic and electrothermal manufactures which are, and must always remain, economically impossible in any other place.

He absolutely differed from Professor Smith in what he said regarding the future minimum cost of electrical energy (5d. per unit).

Professor Smith : I beg your pardon, I meant 0·5d. per unit.

Mr. Ashcroft : Of course that makes a great difference, but Professor Smith's figure is still too high. He knew cases where electricity was sold in bulk, on contract, for ¼d. per unit (equivalent to about £9 per h.p. year), or even half that price, and he knew for certain that ¼d. per unit price could be made to pay the vendors handsomely. But he had in mind something nearer 30s. per h.p. year, for at £9 iron smelting, for example, offered little or no inducement, low-grade sulphide ore treatment became too expensive, and nitrogen fixation was out of the question. But in Norway iron ores can be, and will be, smelted electrothermally at a sooner or later date in virtue of the cheap power and cheap freights—there were no insuperable difficulties in the

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way of establishing such an industry from the engineer's point of view. The same applied to the manufacture of nitrates, which by two different methods were already an established success in Norway, whilst the same industry was not yet established anywhere else in the world. He understood that a company had been formed in one of the Eastern States of America to work the Birkeland-Eyde lime nitrogen process; he doubted whether this would pay there, but it could and did pay in Norway, with power at one-third the price which it is possible to obtain in America, and with cheap fjord-borne carriage.

The figures for steam plant in his Table I. had been criticised. These figures had been worked out some time ago and no doubt might be somewhat open to criticism to-day, but as far as the author could get up-to-date information, they nevertheless represented a fair average. The sizes of the plants in Table I. (replying to Mr. Gaster) were 5,000 kw. He knew that a large Company in Newcastle was supplying electric energy generated by steam plant at prices said to be £5 per kw. year to electrochemical consumers. He could only say he failed to see how this was profitable to the Company, if fair allowances were made on all usual accounts, such as depreciation and also having in view the present prices and known consumption of coal, but even at that price steam-power could not compete in the special fields he was dealing with.

His figures for depreciation in the capital charges for Falls of Class II. had been criticised by Mr. Morrison. But he thought Mr. Morrison could not have clearly grasped his figures, which were ample for the purpose, and more drastic than are usually allowed in calculating steam plants; for if only 3 per cent. were allowed for earthworks—which was sufficient—there was still 5 per cent. for machinery, leaving also a large difference (of 8s. to 10s. per h.p.) for other contingencies, such as debenture interest, royalties, &c.

He would have liked the efficiencies of electric furnaces to have been discussed. The future of electrometallurgy, especially of electrothermal processes, much depended on this point. For instance, what actual thermal efficiency can be obtained from an iron-smelting electric furnace, or again from electric zinc retorts? It seemed to him probable that the latter might be easily more than three times as great as the efficiency of the old retort furnaces, so that the line of economical limitations in this case may be already crossed.

The realisation of the figures in Table II. in practice had been doubted by some of the speakers, but many reliable firms were willing to contract at the figures given, and he knew of several falls nearly as cheap to develop as the one referred to—for example, a fall of 40,000 h.p., from which power could be very profitably sold at 30s. per kw. year. His figures, however, represented a probable average for Norwegian power rates when some of the few excessively cheap powers at present available were snatched up out of the market.

Replying to Dr. Borns, to have reserves of generating plant to take up the load during temporary stoppages—that is to say, duplicating the generating plant—was out of the range of practical politics in electrolytic and electrothermal work. Certainly in connection with the cheap powers in Norway it would seldom prove economical except in a very limited sense—such, for instance, as installing five units of plant and operating four, thus keeping one in reserve. The ice in Norway gave little or no trouble. If a crust of ice formed on the top of the lakes, the water was drawn away from underneath. At Niagara the charge for removing ice from the intakes was a factor to be reckoned with.

He was sorry not to be able to give Dr. Wilsmore any information regarding the Falls of the Upper Nile and the Zambesi.

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NEW APPLICATIONS OF ELECTROMETALLURGICAL ALLOYS.

By AD. JOUVE, Ingénieur-Conseil, Ancien preparateur de Chimie à l'École Polytechnique, Directeur de la *Revue d'Electrochimie et d'Electrométallurgie.*

(*A Paper read before the Faraday Society, Tuesday, June 23, 1908,* PROFESSOR A. K. HUNTINGTON, VICE-PRESIDENT, *in the Chair.*)

Among the alloys prepared by means of the electric furnace the most important are those containing iron, and particularly the ferro-silicons.

Substances prepared in this way have a percentage of silicon varying from 20 to 75 per cent., the most usual being 20 to 25, 50 to 55, and 70 to 75 per cent.

Their uses are well known to all metallurgists, while the analytical methods for determining them are very numerous, accurate, and wholly without complication, being all based on the solutions of the substance in alkalies in the presence of an oxidising agent such as peroxide of sodium, sodium oxide, or free oxygen.

It is a fact well known to analysts that no methods of analysis are based on the effect of acid, except in the case of hydrofluoric acid, for the reason that ferro-silicons with percentages above 20 per cent. are insoluble in acids.

It is this peculiar property, due to silicon alone, which has been employed in an altogether unusual way; *i.e.*, instead of placing ferro-silicons in acids to dissolve them, acids during their preparation may be contained in ferro-silicon apparatus.

Thus, by using high percentage ferro-silicons, apparatus practically unaffected by acids are obtained.

Ferro-silicons are not, however, the only substances which possess this property. For, as this unalterability is due to the silicon, any alloy of a metal with this metalloid will behave in the same way to a greater or less degree according to the nature of the metal. It is evident, for instance, that calcium silicide will be unaffected by acid; the same phenomenon, in fact, occurs, for it is evidently much less affected than metallic calcium would be.

In answer to the question whether the problem of constructing apparatus for the preservation of acids is solved by making use of metallic silicides, it may be said that (1) these substances are very fragile; (2) they contract considerably on cooling, often breaking in the mould when scarcely solid and still at a bright red heat; (3) their melting-point is low compared with the temperatures occurring in ordinary foundry practice—*e.g.*, the second melting in a coke or furnace gas-heated cupola; and (4) certain of these compounds are powerful reducing agents, so that an effect similar to that produced by aluminium may occur. In consequence, fusion in the presence of the air necessary for combustion of the coke or furnace gas is impossible without

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considerably lowering the percentage of silicon (especially in rich ferro-silicons—*i.e.*, about 35 per cent.) to such a point that sometimes it will become as low as 15 per cent., and thus give alloys which are attacked by moderately strong acids.

Manufacture of Apparatus.—It is not proposed to enter here into complete details of the foundry methods employed, which belong rather to technical metallurgy, and it will simply be shown that by quite special and perfect arrangements, as well as by the correction of the mechanical properties with alloys of different natures, it has been possible to obtain, after six years' research, apparatus of all kinds and descriptions.

The first part of the process consists in obtaining melted metal suitable for pouring into moulds.

The simplest and most used of these methods consists in pouring alloys, melted in that apparatus, directly from the electric furnace into a mould lined with some refractory material. The mixture is then made. In a second method, the alloys obtained from the electric furnace are remelted in an oil, or in certain cases in a crucible, furnace and then cast into ingots.

Once the liquid metal is obtained, metals for corrective purposes are added. The number and nature of these is practically infinite for any particular case. They are added directly to the metal in the casting ladle, usually with aluminium, which raises the temperature of the bath and increases the fluidity.

When the ladle is ready it is used mechanically, by a travelling crane, and carried quickly, to prevent cooling, to the mould. The pouring is effected by ordinary means without any special precautions.

The casting is removed as soon as it solidifies, is turned out into the warm casting sand, and thus annealed at a bright red heat. It is then ready for use.

Resistance to Acids.—The resistance of the metallic alloys of silicon, which have been called "Métillures," to acids is quite interesting, as the following examples will show. Nitric acid, even as a vapour, such as is obtained at the exit of a bisulphate retort or when mixed with nitrous acid, does not affect them at all. A striking example of this is given by a pipe which has been submitted for nearly five years to the daily passage of 660 lbs. of nitric acid vapour at temperatures varying from 150° to 200° without its loss in weight exceeding a few decigrammes in a total weight of a score of kilogrammes. This loss occurred quite at the beginning of the period, and was probably due to a few impurities remaining on the inner surface of the pipe after fusion.

Sulphuric acid has still less effect, and acids of strength from 20 to 25, known as *petites eaux*, may be concentrated in vessels of this kind by direct heating and continuous evaporation.

Hydrochloric acid is analogous in its action, and use has been made of pipes of the above material for carrying and condensing its gases.

Acetic acid and the mixture produced by treating calcium acetate with sulphuric acid are without effect on "Métillures," even in the presence of air.

Resistance to other Reagents.—An important English firm has obtained the following figures relating to the resistance of "Métillures" to the action of cyanides, sulpho-cyanides, and prussic acid. The results are very remarkable, for they show both that the unattackability increases with the percentage of silicon, while for a suitable percentage it is practically negligible.

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"MÉTILLURES"—20 PER CENT. NITRIC ACID.

No.	Weight in grms.	Change in Weight.	Reaction with Sulpho-Cyanide.
		After 24 hours.	
1	6·4410	— 0·0392	Violent.
2	5·1669	— 0·0047	Slight.
3	8·1524	— 0·0037	Moderate.
4	14·5013	+ 0·0012	Moderate.
5	1·7060	— 0·0716	Very violent.
6	1·4941	— 0·0034	Very slight.
		After 48 hours.	
1	6·4018	— 0·0207	Violent.
2	5·1622	— 0·0006	Very slight.
3	8·1487	— 0·0032	Moderate.
4	14·5025	+ 0·0045	Slight.
5	1·6344	— 0·0323	Violent.
6	1·4907	— 0·0007	None.

MÉTILLURES—13 PER CENT. SULPHO-CYANIDE OF ANILINE.

No.	Weight in grms.	Change in Weight.	Reaction with Potassium Ferri-cyanide.
		After 24 hours.	
1	6·3811	— 0·0387	Very violent.
2	5·1616	— 0·0065	Moderate.
3	8·1455	— 0·0455	Violent.
4	14·5070	+ 0·0055	Slight.
5	1·6021	— 0·0186	Violent.
6	1·4900	— 0·0160	Very slight.
		After 48 hours.	
1	6·3430	— 0·0675	Very violent.
2	5·1551	— 0·0219	Moderate.
3	8·1000	— 0·0433	Violent.
4	14·5125	— 0·0063	Slight.
5	1·5835	— 0·0216	Violent.
6	1·4740	— 0·0011	Very slight.

Under the same conditions, iron or any other metal in commercial use would be rapidly attacked, thus preventing its employment. The apparatus constructed up to the present time is extremely varied both in form and dimensions, ranging from evaporating dishes, troughs, right-angled bends, elbows, worms, ventilators, &c., and in the other from those weighing about 20 lbs. and having a diameter of 1 ft. to those weighing over 1 ton and measuring 7 ft. across, as well as pipes with a diameter of 8 ft. and weighing about ¾ of a ton.

To sum up, it may be said that the production of a material capable of resisting acids is an accomplished industrial fact, and the principal desiderata are realised. It remains, however, to remedy the unmalleability of these substances. This question is actually being studied, and a solution seems probable in the near future.

As electrometallurgists we may congratulate ourselves that without the electric furnace, which alone permits sufficiently high temperatures for the

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reduction of silicon or silicates by carbon to be obtained, the high percentage alloys of metals with silicon could not have been manufactured.

Further, without the electric furnace the fusion of high-percentage silicides would not have been possible. For when the percentage exceeds 50 the temperature of a coke or gas furnace is not sufficient to permit these alloys to be cast, not because they will not run, but because their specific heat is too low for the metal to be poured. In fact, it will not leave the crucible, but forms a pasty mass.

This latest conquest of the electric furnace has come at a most suitable time. For platinum, the most stable industrial metal, is becoming more and more rare, while its price is increasing by leaps and bounds, making its employment a matter of greater and greater difficulty.

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A REDETERMINATION OF THE ELECTROLYTIC POTENTIALS OF SILVER AND THALLIUM.

By F. J. BRISLEE, D.Sc., Muspratt Laboratory of Physical and Electrochemistry, University of Liverpool.

(*A Paper read before the Faraday Society on Tuesday, December* 15, 1908, Dr. T. M. Lowry *in the Chair.*)

The potential difference between a metallic electrode and a solution containing ions of the same metal is given by the equation—

$$\varepsilon_{electrode} - \varepsilon_{electrolyte} = \text{E.P.} + \frac{RT}{nF} \log C_o$$

where C is the ionic concentration of the solution surrounding the electrode, R the gas constant, T the absolute temperature, F the charge per gram equivalent, and n the valency. The electrolytic potential, E.P., is defined as the potential of a metal against a normal ionic solution of the same metal. The E.P. is measured by employing the calomel or hydrogen normal electrode, and determining the E.M.F. between the electrodes of the combination, metal –solution of known ionic concentration || normal electrode. The measured E.M.F. includes the liquid potential at the junction of the two liquids, which can be calculated, in certain cases, by the Planck formula (*Wied. Ann.* 40, 561, 1890), or as Cumming (*Zeitschr. Elektrochem.*, 13, 17, 1907, and *Trans. Far. Soc.*, 2, 213, 1906) has shown, it can be eliminated in some instances by employing a saturated solution of ammonium nitrate as connecting liquid. The ionic concentration can be calculated from the degree of dissociation given by conductivity or freezing-point measurements, and the value for the E.P. calculated. For room temperature 17° C. the equation becomes—

$$\text{E.P.} = \varepsilon_{electrode-electrolyte} - \frac{0{\cdot}058}{n} \log_{10} C.$$

The E.P. at constant temperature is a constant for each metal, and independent of the nature of the salt employed, but depending upon the solvent. Jahn (*Zeitschr. Physik. Chem.*, 33, 545, 1900) has shown by very exact potential measurements that the degree of dissociation of strongly dissociated electrolytes is not correctly given by conductivity determinations, but Cumming (*loc. cit.*) has shown that, in the case of silver nitrate, the degree of dissociation, calculated in the usual way from the conductivity, is a very exact measure of the dissociation between the concentrations $\frac{1}{2}$ and $\frac{1}{10000}$ normal. In the following research the electrolytic potentials of silver and thallium have been redetermined over a range of concentrations, and in different salt solutions, the ionic concentration being calculated from the conductivity, the most recent conductivity measurements being used for the purpose.

Experimental Part.

The E.M.F. measurements were made by the compensation method, using a Clark Fisher Potentiometer. This instrument is designed for exact E.M.F.

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measurements, and has a range of 3·5 volts and reading to 0·0001 volt. An Ayrton-Mather reflecting galvanometer of the d'Arsonval type was used as a detector, and the Weston cadmium cell as a standard. The cadmium cell was compared with a standard cadmium cell, standardised at the National Physical Laboratory. All measurements were made at room temperature, viz., 17° C., and are given to the nearest millivolt.

Silver.

The silver was prepared from the chloride by fusion with sodium carbonate. The metal was then fused and cast into sticks 3–4 mm. in diameter. The sticks were cut into lengths about 20 mm. long and fused on to copper leads. The electrodes were cemented into glass tubes with marine glue, which was quite unacted upon by the liquids employed, and made water-tight joints. The electrodes were always freshly silvered before use by electrolysis of a silver potassium cyanide solution, then thoroughly washed and allowed to stand, all connected together, in a solution of the same concentration as that used in the subsequent measurements, for at least a couple of hours. Electrodes were also silvered by electrolysis of silver nitrate, and electrodes made of silver-foil and gauze were employed. Electrodes prepared as indicated showed no E.M.F. between each other when dipping into the same solution. The electrode vessels were the half elements described in Ostwald-Luther (*Hand und Hülfsbuch*, p. 377), and were connected through a vessel containing a saturated solution of ammonium nitrate to eliminate the liquid potential (Cumming, *loc. cit.*). In order to prevent the liquid surrounding the electrode from becoming impure owing to the diffusion of the saturated ammonium nitrate, a tap was interposed and measurements made through the closed tap. The calomel decinormal electrode $Hg \mid Hg_2Cl_2 \frac{N}{10} KCl \parallel$ was employed as comparison electrode. The E.M.F. of this electrode being better defined than that of the normal calomel electrode, the mercury is 0·613 volt more positive than the solution (Richards, *Zeitschr. Physik. Chem.*, 24, 37, 1897). The calomel electrode was also protected from contamination by the connecting liquid by means of a tap.

Preliminary measurements of the cell—

$$Ag \mid \frac{N}{10} AgNO_3 \parallel NH_4NO_3 \parallel \frac{N}{10} KCl Hg_2Cl_2 \mid Hg$$

showed that the potential could be reproduced to within two millivolts, using a number of different solutions and electrodes and repeatedly resilvering the electrodes. The current flowed in the cell from the mercury to the silver. The combination gave a constant E.M.F. after standing for about an hour and remained constant for a considerable time, in most cases overnight. The following values were obtained for the E.M.F. of the combination—

$$Hg \mid Hg_2Cl_2 \frac{N}{10} KCl \parallel NH_4NO_3 \parallel \frac{N}{10} AgNO_3 \mid Ag,$$

two electrodes of silver being measured in each case ;

1.	2.	3.	4.	5.
0·4002	0·4002	0·4007	0·4018	0·4016 volts.

A rotating electrode was next measured ; for, as Kistiakowsky (*Zeitschr. Elektrochem.*, 14, 113, 1908) has shown, different values were obtained with certain metals as electrodes when rotating electrodes were employed. The solutions were made up with recently boiled out water and care taken

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to exclude air from the electrode vessel and in some cases hydrogen was passed through the solution during measurement. The results obtained were—

1.	2.	3.	4.
0·4012	0·4012	0·4010	0·4010

practically the same value as that obtained with the stationary electrodes.

Stationary electrodes were used in the subsequent measurements, at least three different cells being measured at each dilution, the three determinations agreeing to within less than 1 millivolt.

The following table shows the results obtained for silver on silver nitrate the concentrations varying from 0·1 to 0·002 gram equivalent per litre.

TABLE I.

Concentrated $AgNO_3$.	$\frac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination in volts.	ϵ *electrode solution* 0·1 N.E. = + 0·613.*	ϵ *electrode solution* H.N.E. = O.†	0·058 log C.	E.P. (*c*).	E.P. (*h*).
0·5	0·663	0·438	+ 1·051	+ 0·774	+ 0·027	+ 1·078	+ 0·801
0·1	0·815	0·400	+ 1·013	+ 0·736	+ 0·003	+ 1·076	+ 0·799
0·2	0·900	0·364	+ 0·977	+ 0·700	+ 0·101	+ 1·078	+ 0·801
0·01	0·924	0·345	+ 0·958	+ 0·681	+ 0·118	+ 1·076	+ 0·799
0·005	0·950	0·328	+ 0·941	+ 0·664	+ 0·135	+ 1·076	+ 0·799
0·0002	0·968	0·305	+ 0·918	+ 0·641	+ 0·157	+ 1·075	+ 0·798

The degree of dissociation is calculated from the measurements of conductivity of $AgNO_3$ by Kohlrausch and Steinwehr (*Ber. kgl. preuss. Akad. der Wiss.*, **26**, 581–587; *Zeit. Elektrochem.*, 8, 628, 1902). The mean value for the E.P. calculated from the above results is 1·076 ± 0·0005 volts, a value in good agreement with the recent determination of G. N. Lewis (*Zeit. Phys. Chem.*, 55, 473, 1906).

A series of measurements was next made, employing silver acetate as electrolyte. The silver acetate was prepared by precipitating silver nitrate solution by a fairly concentrated solution of sodium acetate. The precipitate was three times recrystallised from hot water, and the resulting product, perfectly white and crystalline, was dried in a desiccator in the dark. The degree of dissociation was calculated from conductivity measurements, the limiting value $\mu_\infty = 89{\cdot}4$ at 18° being taken from Kohlrausch and Holborn (*Leitvermögen der Elektrolyte*).

The conductivity was measured at 18° C. by the usual Kohlrausch-Ostwald method and gave the following figures—

Dilution.	Molecular Conductivity at 18° C.	$\frac{\mu_0}{\mu_\infty}$.
0·060	63·68	0·712
0·040	71·48	0·799
0·025	74·00	0·827
0·020	75·96	0·849
0·010	80·13	0·896
0·005	83·93	0·938
0·004	84·62	0·944
0·0025	86·00	0·962
0·0020	86·20	0·904
0·0010	87·44	0·978

* 0·1 N.E. indicates the decinormal calomel electrodes.
† H.N.E. indicates the hydrogen normal electrodes.

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The electrodes were freshly silvered by electrolysis of silver potassium cyanide and of silver nitrate before each measurement. The E.M.F. of the combination—

$$Ag \mid \frac{N}{x} AgC_2H_3O_2 \parallel NH_4NO_3 \parallel \frac{N}{10} KClHg_2Cl_2 \mid Hg,$$

gradually increased until a constant value was reached, in about two hours, which remained constant for a considerable time, and in many cases gave the same value after standing for three days. The following table shows the values obtained for the E.P. of silver in silver acetate solutions.

TABLE II.

Concentrated $AgC_2H_3O_2$.	$\frac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination.	ϵ *electrode* $-\epsilon$ *soln.* 0·1 N.E. = 0·613 volt.	ϵ *electrode* $-\epsilon$ *soln.* H.N.E. = 0.	0·058 log C.	E.P$_c$.	E.P$_h$.
0·060	0·712	0·382	+ 0·995	+ 0·718	+ 0·079	+ 1·074	+ 0·797
0·025	0·827	0·362	+ 0·975	+ 0·698	+ 0·090	+ 1·073	+ 0·796
0·020	0·849	0·358	+ 0·971	+ 0·694	+ 0·102	+ 1·073	+ 0·796
0·010	0·896	0·340	+ 0·953	+ 0·676	+ 0·119	+ 1·072	+ 0·795
0·004	0·944	0·323	+ 0·936	+ 0·659	+ 0·140	+ 1·076	+ 0·799
0·002	0·964	0·311	+ 0·924	+ 0·647	+ 0·157	+ 1·081	+ 0·804

The mean E.P. from all these results is + 1·075 volt ± 0·0013 volt.

Rejecting the last number, viz., + 1·081, the mean is + 1·074 ± 0·0007.

The general mean of all the measurements of the E.P. of silver, in both nitrate and acetate solutions, is + 1·0757 ± 0·0006 volt. This value agrees with that determined by Lewis (*loc. cit.*), and is the most probable value for the E.P. of silver in a solution that is normal with respect to silver ions.

Abegg (*Handbuch der Anorg. Chem.*, Band ii., abt. i., 857) refers to an unpublished research by A. Jacques and gives + 0·796 volt for the electrolytic potential of silver from measurements made in silver acetate solutions.

THALLIUM.

The thallium employed in the following experiments was the thallium puriss supplied by the Litophone Fabrikation, Triebes, and on testing was found to contain only the merest trace of impurity. The thallium was cast into sticks 3–4 mm. in diameter, which were fused on to copper leads and then cemented into glass protecting tubes with marine glue. The electrodes were carefully polished with fine emery-paper and then washed in water and allowed to stand, connected together in a solution of the same thallium salt which was to be used in the subsequent measurements. The thallium nitrate, chloride, and hydroxide employed were prepared from the metal. The nitrate was repeatedly recrystallised and the purity checked by analysis. The chloride was prepared from the nitrate by precipitation, and after thoroughly washing was carefully dried. The hydroxide was prepared by bubbling CO_2 free air through distilled water containing a quantity of metallic thallium in small fragments. In this way a $\frac{1}{10}$ normal solution of thallous hydroxide could be prepared in a few hours. The strength of the thallous hydroxide was determined by titration with standard acid, employing phenolphthalein as indicator.

The first measurements of the E.M.F. of the combination—

$$Tl \mid TlNO_3 \frac{N}{x} \parallel NH_4NO_3 \parallel \frac{N}{10} KClHg_2Cl_2 \mid Hg$$

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gave inconstant values, owing to the solutions becoming alkaline, by the solution of the thallium, forming thallous hydroxide, but by employing boiled-out water, and passing hydrogen through the solution during measurement, consistent values were obtained and the solutions remained neutral. The degree of dissociation of both thallium nitrate and thallium chloride was calculated from the conductivity measurements of Kohlrausch and von Steinwehr (*Ber. d. kgl. Preuss. Akad. der Wiss.*, **26**, 581–587; *Zeitschr. Elektrochem.*, **8**, 628, 1902), the limiting values being obtained from these results, viz., μ_∞ for $TlNO_3 = 127{\cdot}75$ and μ_∞ for $TlCl = 131{\cdot}47$ at 18° C. The degree of dissociation of thallous hydroxide was calculated from Ostwald's determinations (*Lehrbuch der Allg. Chem.*, 771). The current flowed from thallium to mercury in the cell. The following tables show the results obtained—

TABLE III.

Thallium in Thallous Nitrate.

Concentrated $TlNO_3$.	$\frac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination.	$\epsilon_{Tl} - \epsilon_{soln.}$ 0·1 N.E. = 0·613 volt.	$\epsilon_{Tl} - \epsilon_{soln.}$ H.N.E. = 0.	0·058 log C.	E.P$_c$.	E.P$_h$.
0·10	0·78	0·724	— 0·111	— 0·388	0·065	— 0·046	— 0·323
0·02	0·84	0·753	— 0·140	— 0·417	0·100	— 0·040	— 0·317
0·01	0·93	0·775	— 0·162	— 0·439	0·118	— 0·044	— 0·321
0·005	0·95	0·788	— 0·175	— 0·452	0·134	— 0·041	— 0·318
0·004	0·96	0·793	— 0·180	— 0·457	0·140	— 0·040	— 0·317
0·002	0·97	0·813	— 0·200	— 0·477	0·157	— 0·043	— 0·320

The mean value of the E.P. from these results is $-0{\cdot}042 \pm 0{\cdot}001$ volt for 0·1 normal electrode $= +0{\cdot}613$ volt or $-0{\cdot}319$ volt for H. normal electrode $= o$. The next series of determinations were made in thallous chloride solutions, and in order to ensure that the values were constant and could be reproduced, several electrodes were used in each experiment and the solution renewed from time to time. The following values were obtained—

TABLE IV.

Thallium in Thallous Chloride.

Concentrated TlCl.	$\frac{\mu_0}{\mu_\infty}$.	E.M.F. of Combination.	$\epsilon_{Tl} - \epsilon_{soln.}$ 0·1 N.E. = 0·613 volt.	$\epsilon_{Tl} - \epsilon_{soln.}$ H.N.E. = 0.	0·058 log C.	EP$_c$.	EP$_h$.
0·01	0·935	0·773	— 0·160	— 0·437	— 0·118	— 0·042	— 0·319
0·005	0·940	0·788	— 0·175	— 0·452	— 0·133	— 0·042	— 0·319
0·004	0·950	0·796	— 0·183	— 0·460	— 0·140	— 0·043	— 0·320
0·002	0·970	0·813	— 0·200	— 0·477	— 0·157	— 0·043	— 0·320

The mean value from these results is—

$$E.P.(_c) = -0{\cdot}042 \pm 0{\cdot}0004 \text{ volt.}$$
$$E.P.(_h) = -0{\cdot}319 \text{ volt.}$$

An attempt to determine the E.P. of thallium was then made, using thallium hydroxide as electrolyte and using the calomel electrode saturated

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solution of NH_4NO_3 as connecting liquid, but the values obtained for the E.P. decreased with increasing dilution of the thallous hydroxide solution. This was thought to be due to the NH_4NO_3 not eliminating the liquid potential at the junction, or, at any rate, not completely eliminating it, so an indirect method was employed, using a thallium electrode in thallous nitrate as comparison electrode and calculating the liquid potential difference by Planck's formula.

The combination—

$$Tl \mid \frac{N}{200} TlNO_3 \parallel \frac{N}{200} TlNO_3 \parallel \frac{N}{200} TlOH \mid Tl$$

gave an E.M.F. of 0·014 volt, the current flowing from the $TlNO_3$ to the TlOH in the cell. The liquid potential $TlNO_3 \parallel TlOH$ calculated from Planck's formula amounts to 0·017 volt, whence from the value for $Tl \mid \frac{N}{200} TlNO_3$ given above the E.P. can be calculated—

$$E.P. = -0{\cdot}161 - 0{\cdot}017 + 0{\cdot}134 = -0{\cdot}044 \text{ volt},$$

a value fairly close to that obtained above and within the limit of experimental error of this indirect method.

The most probable value for the E.P. of thallium from the above measurements is $-0{\cdot}0425 \pm 0{\cdot}0005$ volt. This agrees with that calculated from the measurements of Neumann (*Zeitschr. Physik. Chem.*, 14, 193, 1894) and Wilsmore and Ostwald (*Ibid.*, 35, 291, 338, 1900).

In conclusion, the author expresses his thanks to Professor Donnan and Dr. N. T. M. Wilsmore for their criticism and advice during the conduct of the above measurements.

DISCUSSION.

Professor R. Abegg (*communicated*): May I add the following short remarks to the account of the very valuable and exact redeterminations of Dr. Brislee?—

1. Dr. A. C. Cumming has himself found, and published in the *Faraday Society Transactions*, that NH_4NO_3 solutions are not applicable for cutting out liquid potentials between basic solutions, in agreement with what Dr. Brislee notices on p. 163.

2. As a member of the "potential committee" of the Deutsche Bunsen-Gesellschaft, I might use this opportunity of expressing the hope that their British colleagues will accept the symbols proposed in 1903 by the Bunsen-Gesellschaft (see *Zeitschrift für Elektrochemie*, 9, 685), and accepted by the 5th International Congress of Applied Chemistry in Berlin the same year. According to this ε_h is the potential counted from the N—hydrogen electrode, ε_c from the N—calomel electrode as *zero*-points, the latter not to be mistaken for the potential numbers formerly used by *Ostwald* and his pupils calculating from the N—calomel electrode as being +0·56 volts. Compare also *Z. f. Elektrochemie*, part 50 (1908), p. 818. The notation of Dr. Brislee does not fully agree with this convention.

Dr. G. Senter asked whether temperature differences might not account for the variations found by the author in his results.

The Chairman said he was not convinced as to the usefulness of mathematical methods of calculating probable errors when applied to actual

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experiments. His experience had been that concordant series of observations were easy to obtain, showing a "probable error" of absurdly small magnitude, but that a subsequent attempt to repeat the observations often gave a fresh concordant series of figures differing widely from that which had first been obtained. The mathematical method had the fatal disadvantage that it entirely neglected the sources of error which persisted throughout a series of experiments and were often far more serious than the mere casual variations in the readings.

Dr. F. J. Brislee (*communicated reply*): In reply to Dr. Senter, it is quite certain that temperature differences do not account for the variations found by the author. The temperature of the solutions was observed at the time of measurement, and it never deviated from 17° C. by more than 0·2° C. The author is in entire agreement with the Chairman in regard to the difficulty of getting two *series* of concordant results, and believes that the repetition of the observations should be the test of reliability of the measurements.

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THE HEATS OF COMBUSTION OF ALUMINIUM, CALCIUM, AND MAGNESIUM.

By F. E. WESTON, B.Sc., and H. R. ELLIS, B.Sc.

(*A Paper read before the Faraday Society on Tuesday, December* 15, 1908, Dr. T. M. Lowry *in the Chair.*)

The values given by various experimenters for the heats of formation of Al_2O_3, CaO, and MgO differ very considerably, as is shown in the following table :—

I. $Mg + O = MgO$—

Heat Evolution.		Authority.
148,000 calories	...	Dr. Strauss, *Minet, Production of Al*, p. 209.
143,300 „	...	Beketoff.
143,400 „	...	*Electrochemical and Metallurgical Industry*, 6–8.

II. $Ca + O = CaO$—

151,900 calories	...	A. Guntz and H. Bassett, jun., *C. R.*, 1905, **140**, 863,864.
131,500 „	...	Thomsen (see L. and B.).
145,000 „	...	Moissan.
131,648 „	...	Dr. Strauss, *Minet, Production of Al*, p. 209.
130,900 „	...	Thomsen.

Guntz used pure Ca and formed pure compounds, from which he determined the heats of solution ; this, of course, introduces complications, leading to various corrections. Forcrand, using pure CaO from $Ca(OH)_2$ and determining heats of solution, obtained the same value as Guntz (*C. R.*, 1908, **146**, 217–220). Thomsen used CaO prepared from calcium nitrate, and Forcrand (*C. R.*, **146**, 217–220) points out that the low value obtained was probably due to impurities ; consequently all values based on Thomsen's results will be low (see also *J. C. S.*, Abst. II., **155**, 1908).

Moissan's result was obtained by direct determination of the heat of combustion, and therefore is less liable to error than those results obtained by indirect means.

III. $2 Al + 3 O = Al_2O_3$—

386,988 calories	...	Dr. Strauss, *Minet, Production of Al*, p. 209.
380,200 „	...	Thomsen (see L. and B.).
392,610 „	...	Richards, *Electrochemical and Metallurgical Industry*, 6–8.

Calculating these results for 1 gram-atom of O, they become 128,996, 126,733, and 130,870 respectively.

On account of the great divergence in the above numbers, experiments were carried out with a view of ascertaining as far as possible which element has the greatest heat of combustion by examining the reducibility of the oxides of aluminium, calcium, and magnesium by the metals Al, Ca, and Mg respectively.

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From the foregoing tables it will be seen that the average value of the heat of combustion of Mg is 145,000 calories, that of Ca is 137,000 calories, and that of Al is 129,000 calories; hence from the theory of greatest heat development Mg should reduce CaO and Al_2O_3, Ca should reduce Al_2O_3 and not MgO, and Al should not reduce CaO or MgO.

Now Goldschmidt (*Minet, Production of Al*, p. 213) has already shown that Al can reduce CaO, and Dr. F. M. Perkin has succeeded in reducing Al_2O_3 by Ca; but it was thought advisable to repeat these experiments in order that a complete comparison could be made between the various reductions when carried out under the same conditions.

Experimental.

Series I. The Action of Al Powder upon Al_2O_3, MgO, and CaO respectively.

The Al powder was the same as that used by the authors in their previous work (see *Trans. Far. Soc.*, vol. iv., 1, 1908). The Al_2O_3 was prepared by ignition of pure ammonia alum. The MgO was made by ignition of precipitated magnesium carbonate, and was heated for some hours in a muffle at 1,000° C. and was in an extremely fine state of division. The CaO was obtained by ignition of marble, finely powdered, passed through a 40,000-meshed sieve, and the resulting powder again heated at 1,000° C. for one hour.

1. $Al_2O_3 + 4\,Al$. This experiment was first carried out by Duboin (*C. R.*, cxxxii., No. 13). The mixture readily reacts with a fuse, forming a blackish-grey product which dissolves in HCl with the evolution of H; it contains, probably, a suboxide of aluminium, but very little nitride.

2. $2\,Al + 3\,CaO$. The mixture, contained in a Hessian crucible, would not react in the cold, even when a fairly large fuse was used; when heated over a bunsen burner for two hours (the bottom of the crucible was at a dull red heat), a fuse again brought about no reaction. The crucible was then placed in the muffle at its hottest part; after two minutes, the crucible then being bright red, action started at the surface and then very rapidly spread throughout the whole mass, giving a somewhat violent reaction. The reaction consisted first of the oxidation of the surface Al by the air, and the heat produced by this reaction, together with the heat supplied by the furnace, brought about the reduction of the CaO by the Al; this reaction appears to us to be endothermic, since it was only possible to bring about the reaction under the conditions stated. The product of the reaction consisted of a hard, black, fused mass, and contained free Ca, calcium aluminate, free Al (and possibly some Al_2O), Al_2O_3, and CaO; it also contained a small amount of nitride and carbide.

Estimation of Free Ca and Al.—The finely powdered substance was treated with cold water and the gas evolved collected and analysed. From volume of H evolved the percentage of free Ca was calculated; a small quantity of C_2H_2 and CH_4 was found present. After treatment with water, HCl was added and the process repeated.

Per cent. free Ca = 8·3
„ „ free Al = 6·1
„ „ nitrogen = 0·375
(as nitride)

Hence it is evident that Al powder can reduce CaO at high temperatures, and it is probable that the reaction $2\,Al + 3\,CaO \rightleftarrows 3\,Ca + Al_2O_3$ is a reversible one and that a stage of equilibrium is reached under the above conditions.

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3. 2 Al + 3 MgO. The reduction could not be brought about even at the highest temperature attainable (*e.g.*, about 1,100° C.); the only change obtained was a superficial oxidation of the Al; the contents of the crucible were otherwise unacted upon.

Hence it appears that the heat of formation of MgO is greater than that of CaO.

Series II.

1. $3\,Ca + Al_2O_3$. The calcium was first converted into fine shavings in a lathe, and these were then crushed as small as possible in an iron mortar, and that portion which passed through a 120-meshed sieve was used.

The mixture, in a Hessian crucible, would not react in the cold even when a moderately large fuse was used, but on heating with a bunsen burner until the bottom of the crucible was at a dull red heat, a violent reaction took place and the larger portion of the contents of the crucible was ejected. From the way in which the reaction took place it is fair to assume that if calcium powder in a sufficiently fine state of division were employed the reduction would take place readily in the cold, and if air were excluded and sufficiently large quantities of mixture employed, fused Al could be obtained (see also Dr. Perkin, *T. F. S.*, iii., **3**, 184). In this reaction the Al produced probably volatilised, and consequently oxidised under the very high temperature obtained, and this may account for the small percentage of Al found and also for Dr. Perkin's failure to obtain globules of metallic Al. The authors intend repeating this experiment under such conditions as to avoid loss, &c.

The presence of free Al was shown by treating the finely powdered product with water until no more gas was evolved, even on heating, and then adding HCl; a rapid effervescence of H took place, and Al was found in the solution. The product contained about 8 per cent. of free Al.

2. Ca + MgO. The mixture, placed in a Hessian crucible, was found to react slowly when the surface was heated with a bunsen burner; the surface Ca ignited, and the incandescence *slowly* spread throughout the mass from the top downwards. On cooling the contents of the crucible were found to be white at the top to a depth of about $\frac{1}{8}$ inch, and then of a deep yellow.

It was thought at first the action was due to reaction of the Ca with the atmosphere forming a small amount of lime and a large amount of calcium nitride. That this was not so was evident from (1) the analysis of the resulting mixture; (2) that the calcium when heated in a crucible by itself under the same conditions only burnt on the surface and remained unchanged below; and (3) a mixture of CaO and Ca when treated in the same manner or even when strongly heated by a Bunsen flame only reacted at the surface.

Analysis of the product gave—

N as nitride	= 5·79	per cent.
Free Ca	= 4·16	„ „
„ Mg	= 0·58	„ „

It was not possible to decide whether the nitride was calcium nitride or magnesium nitride or a mixture of both. But from the large percentage of nitride (about 30 per cent. if calcium nitride) it appears that the atmospheric N plays a great part in the reaction observed.

Series III.

1. Mg + CaO. That Mg will readily reduce CaO in the cold is, of course well known, this reaction serving for the preparation of argon from the air. A mixture made in the proportion Mg + CaO can easily be fired by a lighted

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match, the reaction proceeding steadily throughout the mass. The resulting product is of a bright yellow colour, and consists chiefly of calcium nitride.

Analysis of product gave—

Ca_3N_2 = 33·65 per cent.
Free Ca = 1·29 „ „
„ Mg = 0·47 „ „

In this reaction, in order to obtain a yield of Ca, air would have to be excluded.

2. $3\,Mg + Al_2O_3$. This mixture, in a Hessian crucible, easily reacted with a fuse; the reaction was somewhat violent, the mass swelling up considerably. The resulting product was quite black.

Analysis of product gave—

N as nitride = 7·43 per cent.
Free Al = 0·71 „ „
„ Mg = 3·87 „ „

In this reaction, as in the case of Ca and Al_2O_3, it is probable that most of the Al liberated is converted into nitride and some re-oxidised to Al_2O_3.

Although in these experiments, which were only carried out on a small scale (20 to 50 grams), complications arise partly from the interaction of the various hot metals with the air and with the oxides, it is quite evident that both Mg and Ca reduce Al_2O_3 in the cold and also that Mg easily reduces CaO with the formation of the free metal.

It is thus evident that the heat of combustion of Mg is greater than that of Ca, since MgO is not reduced by Al, whilst CaO is at a very high temperature; however, the heat of combustion of Mg is not much greater than that of Ca, since it is possible to cause Ca to interact with MgO; also the heats of combustion of Mg and Ca are much higher than that of Al.

The partial reductions of CaO by Al and of MgO by Ca—probably endothermic reactions—are analogous to the reduction of B_2O_3 by K and Na respectively. Gay-Lussac prepared B by heating B_2O_3 with K to a red heat in an iron tube. Now, the heat of combustion of B to B_2O_3 is given as 317,200 (Troost and Hautefeuille-Watts, *Dictionary*), 314,821 by Roscoe and Schorlemner; whilst the heat of combustion of K to K_2O is given by Beketoff as 97,100 (L. and B.), 86,800 by Rengarde (*J. C. S.*, Abs. II., **156**, 1908), and 84,800 (*ibid.*).

Hence $B_2O_3 + 6\,K = 3\,K_2O + B_2$ becomes thermally (using average values)

$$-[(316{,}000) - 3\,(89{,}500)]$$
$$i.e. = -47{,}500;$$

i.e., heat must be supplied; a similar reaction occurs with Na.

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DISCUSSION.

Dr. H. Borns: Though Mr. Weston has stated that he is repeating his experiments *in vacuo*, I cannot but point out that experiments such as shown —interesting certainly in themselves—cannot decide anything about the uncertain heats of formation of the oxides of Al, Ca, Mg. Mr. Weston is

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working in air; he powders his metals, the mixtures possibly stand for hours, and I doubt that his metal is free of oxygen when he starts his experiment. Electrolytic calcium shavings turned on a lathe would hardly be free of oxide. As Mr. Weston starts his combustion with a piece of magnesium wire, the ammonia might possibly be due to magnesium nitride in all these cases. The observation of the influence of $CaCO_3$ is interesting with regard to the formation of calcium cyanamide. It is well known that carbide and nitrogen alone will hardly yield any cyanamide; we want the presence of some other substance to render the process remunerative, and several investigators have mentioned $CaCO_3$ among the recommendable additions, of which $CaCl_2$ is most generally employed. As that reaction has not sufficiently been explained so far, this observation of Mr. Weston's deserves attention. If Mr. Weston performs his experiments in air, however, the presence of some carbonate would generally have to be assumed in the Ca and CaO tests.

Mr. H. K. Picard said he had assisted Mr. Vautin in 1893 and 1894 in his early experiments, which formed the foundation of what was now known as the "thermit" process, and he had occasion to carry out reductions of a large number of oxides and sulphides by means of aluminium. As far as he had gone he had reached the same conclusions as the author. They succeeded, for example, in producing calcium by the reduction of lime with aluminium, but they failed to reduce magnesia. They had not tried the reverse reduction of alumina by calcium, and he was much interested to learn that this was possible at the temperature of a muffle furnace.

An interesting reaction to study would be that between alumina and aluminium sulphide. He saw no reason why such a reaction should not take place, although he had not succeeded in bringing it about himself—he always was troubled by the formation of what he believed to be a suboxide of aluminium. He hoped the authors would try it, because it might prove to be a possible method of manufacturing aluminium.

Mr. H. R. Ellis: In the reductions when magnesium was employed it is evident from the following considerations that the nitride obtained was not magnesium nitride.

In the first place, when magnesium burns in air very little nitride is produced, and when magnesium reduces the oxide of a metal which does not form a nitride only a very small amount of nitride is produced.

Now, magnesium nitride readily burns to magnesium oxide if it is heated, consequently when magnesium burns in air, since a very great heat evolution takes place, any nitride produced would be destroyed, and when magnesium powder reduces an oxide which has only a small heat of formation such would likewise be the case, *e.g.*—

$$\underset{37{,}000}{CuO} + \underset{148{,}000}{Mg} = MgO + Cu + 111{,}000.$$

The heat evolution when Mg reduces CaO is not very great—

$$\underset{145{,}000}{CaO} + \underset{148{,}000}{Mg} = MgO + Ca + 3{,}000 \text{ cals};$$

(Moissan's value)

consequently, we might expect that the nitride is present as magnesium nitride, but the following considerations render this unlikely.

When the amount of Mg is in excess the amount of nitride increases but

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is never more than the Ca can account for ; and again, SrO and BaO with a much greater heat evolution on reduction give a larger yield of nitride.

Again, when B_2O_3 and SiO_2 are reduced by Mg the yield of nitride is very small, and in both these cases the heat evolution is not very great—

$$\underset{316,000}{\tfrac{1}{3}\,[B_2O_3} + 3Mg = \underset{444,000}{3MgO} + B_2] + 42{,}600.$$

Every mol. of MgO formed liberates 42,600 cals.

$$\underset{215,690}{\tfrac{1}{2}\,[SiO_2} + 2\,Mg = \underset{296,000}{2MgO} + Si] + 20{,}000.$$

Every mol. of MgO formed liberates 20,000 cals.

Dr. N. T. M. Wilsmore agreed with previous speakers that the reactions were too complicated to allow of deductions of or from the heats of formation of the simple oxides. Assuming with the authors that lower oxides were formed, which, unless the air took some notable part in the reactions, seemed to be the only explanation possible of the phenomena described, the heats of formation of these lower oxides would be determining factors in the changes observed. For as all the heats of formation involved were probably high, they might be taken to be roughly proportional to the free energy changes. He looked forward with interest to the promised experiments in absence of air. Answering Dr. Borns, he thought that metallic calcium was nearly as stable as metallic magnesium.

Mr. F. E. Weston : In reply to Dr. Borns I should like to state that the magnesium ribbon used in the experiments shown at the meeting was simply a convenient means of starting the reaction, *i.e.*, an easy means of heating up the mixture ; in the experiments described in the Paper the action was started without magnesium, and yet nitrides were formed.

That lime, left exposed to air, readily takes up CO_2 is well known, and hence the authors took precautions that the lime used was free from CO_2. It is hardly likely that the calcium contained oxide, since the turnings used were extremely bright ; calcium is much more stable than is usually supposed ; pieces of calcium turned up in a lathe possess a high metallic lustre which remains unaltered for days when kept in an airtight dry bottle.

The authors are quite aware of the weakness of the deductions drawn from their experiments, due to the probable interaction of the air ; but since all the experiments were carried out under the same conditions, the same error would affect all to the same extent, and hence the results are comparable. The only error which is not common to all the experiments is the one pointed out by Dr. Wilsmore, namely, the heat changes due to the formation of low oxides; this error undoubtedly affects some of those reactions in which Al or Al_2O_3 takes part.

The authors, however, hope to state in a subsequent Paper what part the atmosphere plays in the reactions described, since experiments are now in progress in which the reactions are being studied *in vacuo*.

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THE FORMATION OF GRAPHITE BY THE INTERACTION OF MAGNESIUM POWDER AND CARBONATES.

By H. RUSSELL ELLIS, B.Sc., F.C.S.

(*A Paper read before the Faraday Society on Tuesday, December* 15, 1908, Dr. T. M. Lowry *in the Chair.*)

Winkler, in an investigation of the action of magnesium on the carbonates of the alkaline earths, showed that the carbonates were readily reduced on heating, and amorphous carbon was produced in the reaction.* The properties of this carbon were not investigated by Winkler or by Maquenne, who also studied the reaction between magnesium and the alkaline earth carbonates.

During an investigation of the action of magnesium powder on various carbonates quantities of carbon were produced, and the object of the present Paper is to show that this carbon is a mixture of amorphous carbon and graphite; in some cases it consists almost entirely of graphite. The graphite is non-intumescent.

A mixture of a carbonate and magnesium powder does not require heating before action commences. If such a mixture be ignited in one portion by a match or by means of burning magnesium, a reaction similar to Goldschmidt's occurs, and proceeds throughout the whole mass more or less vigorously; in many cases CO is evolved, which causes much of the contents of the crucible to be ejected; if the metal is of comparatively low boiling-point, this distils off and burns and so renders the reaction more violent. Since this reaction was accompanied by very high temperature, and since at high temperatures graphite is the stable form of carbon, it was thought that the carbon would be present in this form. In all cases this was found to be so, although amorphous carbon was also present, the graphite being formed as such or formed from amorphous carbon at the extremely high temperature of the reaction.

Detection of Graphite in the Reaction Products.

The contents of the crucible, after a reduction had taken place, were boiled for some time with hydrochloric acid, washed, filtered, and dried, and then treated with fuming nitric acid prepared from boiled sulphuric acid, dry potassium nitrate, and dry potassium chlorate. The mixture was kept cold at first and then placed on a water bath and the temperature slowly brought to 100° C. and the solution evaporated to dryness. If the mixture be made at a high temperature, explosion occurs, and at times the whole mass inflames; by mixing in the cold and warming as described above, in no case was any explosion produced. Small quantities only were used; in nearly every case a deep green coloration was produced at the first treatment, and a yellow powder was left after dissolving the humic acids and potassium chloride in the dry residue; if any black powder was left, this was dried and again treated with the oxidising mixture. The complete conversion

* *Ber.* xxiii. 2,642, 1890; see also Moissan, *Electric Furnace*, p. 38.

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of the carbon into humic and graphitic acid seldom required more than one treatment. The graphitic acid obtained readily exploded on heating, forming pyrographitic acid.

Estimation of the Amounts of Graphite and Amorphous Carbon in the Mixture.

In Berthelot's memoir on carbon,* it was shown that fuming nitric acid attacked amorphous carbon, producing humic acids which were soluble in water and did not attack graphite. This observation has served as the basis of a method of estimating graphite and amorphous carbon in a mixture of the two.

The total ash is estimated in the mixture by ignition in the muffle furnace; the amorphous carbon quickly burns away, whilst the graphite remains for some time and only slowly burns. Another portion (0·1–0·4 gr.) of the mixture is heated on a sand bath in a conical flask with fuming nitric acid for several days until no more brown fumes are evolved, fresh additions of nitric acid being added from time to time. After the oxidation is complete the solution is poured out into an evaporating basin and evaporated to dryness on the water bath to remove all the nitric acid. The residue, consisting of humic acid, graphite, and insoluble mineral matter, is extracted with water and filtered through a tared filter-paper, washed, dried, and weighed. It is then finally burnt in the muffle, the loss of which gives the amount of graphite present. It is essential that the nitric acid be removed, as the mixture is difficult to filter and the filter-paper is attacked.

The method was tested by using a mixture of pure graphite † and amorphous carbon, and it was found to give fairly good results, the graphite being 1–2 per cent. too high, probably owing to the great difficulty of removing traces of moisture.

This method is very tedious and requires much time, so it was not considered worth while to estimate any of the mixtures obtained. Graphite was obtained from the carbonates of the alkaline earths—ammonium carbonate, cadmium carbonate, and magnesium carbonate—and by the action of magnesium on carbon dioxide.

Reduction of Carbonates of Barium, Calcium, and Strontium.

Mixtures were made in the following proportions:—

(*a*) $RCO_3 + Mg$,
(*b*) $RCO_3 + 2\,Mg$,
(*c*) $RCO_3 + 3\,Mg$,
(*d*) $RCO_3 + 4\,Mg$,
(*e*) $RCO_3 + 3\,Mg + 2\,C$,
(*f*) $RCO_3 + 3\,Mg + 6\,C$,

and the reaction carried out in open crucibles and in closed iron tins at high temperatures.

In all cases the reaction was violent, especially when carbon was initially present, and in all cases graphite was found in the products of the reaction; in the case of reactions (*c*) and (*d*) very little amorphous carbon was produced.

The reaction between barium and strontium carbonates and magnesium powder when carried out in open crucibles always produced the carbide, nitride, and large amounts of cyanide; when the reaction took place in

* *Ann. de Chim. et de Phys.*, ser. 4, xix. 392, 1870.
† *Trans. Far. Soc.*, vol. iv., pt. 1, p. 70.

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closed tins, the carbides only were produced. With calcium carbonate no carbide, nitride, cyanamide, or cyanide was produced when open crucibles were used; when the reaction took place at high temperatures in closed tins, calcium carbide only was produced. Since results differing from those of Winkler and Maquenne were obtained, a subsequent Paper on this subject will be given.

It is well known that most carbides dissolve carbon and deposit them in the form of graphite; that the graphite was not obtained in this way is evident from the fact that the mass had not a fused appearance, but was a very soft powder.

Action of Magnesium on Ammonium Carbonate, Magnesium Carbonate, and Cadmium Carbonate.

The action was vigorous and produced graphite, but no nitride, cyanide, or carbide.

Action of Magnesium on Carbon Dioxide.

A rapid stream of dry carbon dioxide was passed over 25 gms. of dry magnesium powder, and this was heated strongly at one point.

After a time the magnesium caught fire and burnt rapidly, producing a black and white residue. This powder was treated with hydrochloric acid and the carbon filtered and dried; about 2·5 gms. were obtained. Only a very slight amount of carbide was formed, no gas being evolved when the powder above was dropped in water; the smell of acetylene, which is very easily observed from minute quantities of the gas, was, however, noticed.

The black powder contained graphite, but only in small quantity.

Percentage of ash	... ...	= 6·64
„ graphite	... ...	= 12·09
„ amorphous carbon	... ...	= 81·27

The reaction in this case is comparatively slow, and the mixture was spread out over a long tube and consequently no very high temperature was attained; on the other hand, when the reduction takes place in crucibles, the heat is concentrated, and a much higher temperature results and more of the carbon is changed into graphite.

It seems probable that amorphous carbon is first produced by the action of the magnesium on the carbonate, and that more or less of this is converted into graphite owing to the enormous heat evolved.

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COLLOIDAL BARIUM SULPHATE.

By ERNEST FEILMANN, B.Sc., Ph.D., F.I.C.

(*A Paper read before the Faraday Society, Tuesday, December* 15, 1908, DR. T. M. LOWRY *in the Chair.*)

PRELIMINARY COMMUNICATION.

Descriptions of the preparation of colloidal barium sulphate are comparatively rare; G. Buchner (*Chem. Ztg.*, **17**, 1893, 878) describes the precipitation of a gelatinous form of this substance on mixing concentrated aqueous solutions of barium acetate and aluminium sulphate, but on dilution or on standing this reverts to the ordinary form. Neuberg and Neumann (*Biochem. Zeit.*, **1**, 1906, 166) obtain it by the addition of aqueous sulphuric acid to a methyl alcoholic solution of barium hydroxide, as a jelly which forms a porcelain-like mass on ignition. v. Weinarm (*Zeit. f. Chem. u. Ind. d. Kolloide*, 1908, **2**, 89) describes the preparation of numerous salts of the alkali earth and alkali metals, including barium sulphate, in the form of jellies. Some years ago the author of the present communication experimented on the protective action of alkali-casein solutions in the production of colloidal solutions of organic and inorganic substances. For various reasons these were not published at the time; the most various substances, including many of the heavy metals and their more insoluble salts, were thus obtained in solutions of great strength and somewhat surprising stability, and it was thought that a description of such a solution and its method of preparation might not be without interest, especially in view of the ready accessibility in large quantities, and cheapness, of the materials employed.

Twenty-three grms. of commercial casein were dissolved at below 40° C. in water containing 0·09 grms. of sodium hydroxide and diluted to 230 c.c. To this solution was added a solution of 14·2 grms. (0·1 mol.) of anhydrous sodium sulphate in water to 200 c.c. To this mixed solution a solution of 24·5 grms. (0·1 mol.) of crystallised barium chloride in water to 100 c.c. was then slowly added at 20° C. with vigorous stirring. A thick, creamy, and almost homogeneous liquid was so obtained, though there was a certain amount of sedimentation on standing. It was precipitated by adding 12 c.c. of glacial acetic acid, which caused the formation of a white, curd-like precipitate, allowed to stand, and the precipitate washed by repeated decantation till free from acid reaction. It was then stirred with 400 c.c. of water and 2 c.c. of 15 per cent. sodium hydroxide solution at 40° C. for three hours, filtered through an open paper filter and evaporated to dryness on the water-bath. Before evaporation the liquid had much the appearance of ordinary milk by reflected light; by transmitted light it was transparent in thin layers, showing the peculiar reddish-yellow tinge so characteristic of many colloidal solutions. The solid obtained by evaporation was translucent, and of a horny appearance and texture. It was quite soluble in water to a similar solution to the one just described, but on standing it appears to undergo some slight change which renders it necessary to employ a very little dilute alkali in order to obtain a perfect colloidal solution. On ignition 56·7 per cent. of barium

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sulphate was left. After keeping for six months 2 grms. of the substance dissolved in 70 c.c. of water and 0·5 c.c. of normal sodium hydroxide solution, leaving only a negligible amount of residue. Under a magnification of 200 diameters particles in rapid movement can just be made out under the microscope, and the appearance of the liquid under magnification is much the same as that of the colloidal solutions of tungsten prepared by Kuzel's method. The solutions are very stable; only a slight amount of sedimentation takes place after standing for many hours, and this is very possibly due to the action of the air, which appears in some way to affect the stability of the solution.

The protective action of organic and other colloids in cases such as the one just considered is one that has not yet been adequately explained, though the phenomenon has been known for a very long time. Some light is thrown on this question by the experiments of Michaelis and Pincussohn (*Biologische Zeit.*, **2**, 251), who experimented with colloidal suspensions of indophenol and mastix. These were more stable than suspensions of indophenol alone, and microscopic and optical examination of the mixture led to the conclusion that each particle of indophenol was surrounded by a layer of mastix. There is reason to suppose that the colloidal barium sulphate and other preparations of the present author are in a very similar condition, and that each particle of inorganic material is surrounded by a layer of casein; they behave towards acids and alkalies in a very similar manner to casein itself, being precipitated by the former from solution and redissolved by the latter, and this process can apparently be carried on alternately almost *ad libitum*. These facts suggest that the surface in actual contact with the liquid media consists of casein only, and that it is this surface which conditions the stability of the solutions obtained. This view is also in accordance with the fact that a certain minimum quantity of casein is in each case necessary to hold the inorganic substance in solution.

DISCUSSION.

Dr. V. H. Veley (*communicated*): The preliminary communication of Dr. Feilmann on colloidal barium sulphate presents various interesting points, and it is hoped that the author will continue his investigations upon this subject, using other colloidal menstrua, such as gelatine, agar-agar jelly, various albumens, &c.

From the description given of the liquids as having "the appearance of ordinary milk by reflected light," it would seem that they were of the nature of emulsions (*cf.* Ramsden, *Proc. Roy. Soc.*, 1903, **72**, 156, and Pickering, *Journ. Chem. Soc. Trans.*, 1907, 2001), and their general behaviour is very similar to that of those described by the last writer. It would be a further point of interest to examine more fully the size of the barium sulphate particles under a microscope of high power, preferably using a hot stage according to usual bacteriological methods.

Some time ago the writer had occasion to examine the size of barium sulphate particles precipitated from barium chloride and a sulphate without addition of free acid (which makes the precipitate more crystalline and coarser grained); the powder was subsequently ignited and sifted through fine muslin (*Journ. Chem. Soc. Trans.*, 1903, 749). The average diameter of the particles was found to be 1–2 μ (= 0·001 to 0·002 mm.), and their edges were perfectly sharp and well defined. It appears probable that particles of barium sulphate in the colloidal condition would be larger and without definite edges.

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By arranging matters so that the organic menstruum could be slowly melted off, the appearance of the barium sulphate under the microscope could be ascertained, and the temperature at which the salt passes from a colloidal to a crystalline condition could be determined within a few degrees of temperature.

The conditions of precipitation by acids, and resolution by alkalies, could similarly be studied, and thus more information obtained as to the relative size of the particles according to the nature of acid or alkali used and their respective concentrations.

Another line of investigation might be to determine the size and form of barium sulphate particles by a repetition of the experiments of Lodge (*Brit. Assoc. Report*, 1884, 309), varying the conditions of tube-diameter, potential gradient, and current, as it appears possible that every variety from well-defined crystals to amorphous masses of barium sulphate could thus be obtained.

Professor W. W. Haldane Gee (*communicated*): Since the work of Graham in 1861, colloidal chemistry has, chiefly by the efforts of German investigators, been much extended in its scope. It now promises to become a very important branch of physical chemistry, and to be fertile in technical applications. Dr. Feilmann's communication is to be welcomed more especially as a contribution on the protective action of organic colloids in producing stable colloidal solutions. This action, which has been much studied by Zsigmondy and others, has not, as the author states, been completely explained. The particles seem to be coated by the protector. This is in accordance with the fact shown by Quincke, that if we have three immiscible liquids A, B, and C, then B will tend to form a layer separating the other two if—

$$T_{AB} + T_{BC} < T_{AC},$$

where T_{AB} is the surface tension between A and B, whilst the other quantities are corresponding values for the other boundaries.

It has been suggested that the coating may form a permanent electric "double layer," with the effect of preventing the neutralisation of the nucleus by ions of an opposite charge.

It would be interesting to extend the method described to the salts of calcium. Using albumen and like substances, much might be learnt about the method in which dentine and other hard substances are produced in animal tissues.

Dr. G. Senter said that although the title of the paper was "Colloidal Barium Sulphate," he understood from the author's statement that he regarded the system as made up of particles of ordinary barium sulphate surrounded by a skin of casein, and he himself quite agreed with the author that the results were best accounted for in this way. This view might perhaps be tested by grinding the coagulated precipitate with finely-divided sand, with the object of breaking up the particles, and then examining as regards solubility. An ultra-microscopic examination of the particles should also prove of interest. The proportion of casein was rather large; was it not possible to obtain complete solution with relatively less casein?

Dr. H. Borns: The remarks I intended to make concern the point already alluded to by Dr. Senter. In the experiments of Neuberg and Rewald on colloidal salts of the alkaline earths, there is no colloidal envelope for the particles of an organic substance. They dissolve barium oxide in aqueous methyl-alcohol, pass CO_2 through the solution, and obtain a gelatinous solution which, as long as some methyl alcohol is left in it, will completely redissolve in water. With sulphuric acid this solution gives colloidal barium

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sulphate, but I do not remember whether that sulphate will completely redissolve likewise. As regards a possible application of those colloids, I might mention the street photometer of A. Wright, shown recently at the exhibition of scientific apparatus arranged by the Physical Society. A copper sphere is coated inside with barium sulphate to provide a light-reflecting surface; that coating might more easily and uniformly be produced with Dr. Feilmann's colloidal sulphate than with ordinary sulphates, I should think.

Dr. C. H. Desch suggested that as alkalies peptonised the coagulated colloid, this was rather against the existence of the $BaSO_4$ itself in a colloidal condition, since colloidal $BaSO_4$, coagulated by acid, would not be taken up again by alkali. Dr. Feilmann's suggestion that small particles of $BaSO_4$ are merely enclosed in colloidal envelopes of casein was probably right.

He called attention to the work of von Weimarn, who has shown (*Zeitschr. für Kolloide* and *Journ. Russ. Phys. Chem. Soc.*) that the so-called "amorphous" precipitates of $BaSO_4$, &c., are probably minutely crystalline, and has photographed the stages of their growth.

Dr. Feilmann (*in reply*) was much obliged to Dr. Veley for his very valuable suggestions, but was afraid that to carry them out at all adequately would imply a very considerable amount of work. Pickering's results were, in the author's opinion, in no way analogous to his; Pickering's emulsions were very much coarser in texture and he obtained a system of oil globules surrounded by a layer of powdered solid, so that there was a liquid nucleus surrounded by a solid envelope, whereas the properties of the liquids described by the author all pointed to the presence of solid nuclei surrounded by a liquid, or semi-liquid, envelope. Also, of course, Pickering's emulsions were destroyed completely by the application of heat, whilst the author's liquids could be evaporated to dryness, and the solid so produced could be re-dissolved to a liquid of the same character as before. In other characteristics, also, such as viscosity, the preparations of Pickering and of the author showed very different characteristics. In reply to Dr. Senter, he had referred to the system as a whole as a "colloidal solution" in deference to the generally accepted nomenclature; from the work of v. Weimarn it was doubtful whether the term "colloidal," as applied to a minute particle, had any very definite meaning. He had hoped to get some insight into the nature of the protective action of colloids—this appeared to him to be the really interesting question. He would certainly try grinding up with sand, but was not very sanguine as to the result. The quantity of casein used was the minimum with which he had succeeded in preparing stable preparations of barium sulphate. It took a very exceptionally large amount, probably owing to its very crystalline character. Other inorganic solids, such as silver, could be converted into pseudo-soluble preparations containing very much smaller proportions of casein, and the author hoped to publish further results on the subject shortly. As a result of his work, he had come to the general conclusion that the greater the tendency of a substance to crystallise, the more of the protective colloid was needed in order to produce a stable hydrosol. He was much obliged to Dr. Borns for his suggested application of the material; he hoped to extend his investigations to other protective colloids, as suggested by Professor Haldane Gee and Dr. Veley.

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APPLICATION OF ELECTROLYTIC CHLORINE TO SEWAGE PURIFICATION AND DEODORISATION BY THE "OXYCHLORIDES" PROCESS.

By SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C., F.C.S.

(*A Paper read before the Faraday Society, Tuesday, February* 9, 1909, Dr. V. H. VELEY, F.R.S., *in the Chair.*)

SECTION I.—THE APPARATUS.

The first electrolyser of the Oxychlorides Company was a semicircular wooden trough lined with graphite on a metallic base which formed the anode. In this trough revolved the cathode, a wooden cylinder covered with lead, attached to a copper ring with a rubbing contact-block. The two poles were connected with the terminals of a low-potential dynamo. The later form of electrolyser is of larger size, and the cross-section is completely circular except as to about 4 in. at the top, which is left open for the free escape of gases evolved in the electrolysis. Both machines occupy the same floor space, and have respectively an electric surface of 30 and of 57·5 square feet. The graphite blocks are of the highest grade Acheson make, treated at the Oxychloride Works by a process which adds materially to their life as electrodes, so that a small machine has been in constant use at a distillery for four years without repairs, and is still carrying its full current.

This form of electrolyser gave satisfactory results in some directions, but in applying the process to bleaching of cotton, linen, and paper-making material, it was found that the salt consumption was too high, and that loss occurred in circulating the solutions from electrolysers to bleaching vessels and *vice versâ*.

To meet these conditions it was decided to produce a more concentrated solution by using a diaphragm, and after some months of experiment the Company have succeeded in obtaining a diaphragm which has a commercially long life, gives a good current efficiency, and does not set up too much resistance. This diaphragm machine shows results in the following figures supplied by the Oxychloride Company. With a current of 1,500 amperes at 4·6 to 5 volts, according to density of salt solutions, the current efficiency in available chlorine at end of continuous daily runs of eight and ten hours was 68 per cent. The daily salt consumption was 90 lbs. It is, of course, essential that the salt solutions be purified.

In the earlier runs of this apparatus it was found that chlorate was formed in the anode chamber equivalent to 9·5 to 12·5 per cent. of the current efficiency in av. Cl, but further experience showed that this formation of chlorate could be minimised, and also that the salt consumption could be still further reduced. It appears that ultimately the chlorate in the anode chamber will not exceed the equivalent of 3 per cent. of the current efficiency in av. Cl, with, of course, a corresponding increase in percentage of available chlorine, and without raising the voltage. I may mention that in tests of the

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liquid as used at Guildford I have found over 8 per cent. of av. Cl and have not found chlorate.

The main advantages resulting from this diaphragm machine are—

Elimination of the circulation of electrolyte.
Reduced quantity of electrolyte handled daily, thereby reducing cost of labour and power.
A less salt consumption.
Increased production per horse-power hour.
Reduced cost per kilogramme of av. Cl.

The degree of concentration in av. Cl is purely a matter of manipulation, and up to 15 per cent. av. Cl calls for no special care.

Whilst the diaphragm machine was essentially developed for bleaching and allied trades, it is equally applicable to sewage treatment, and a merit of the new solution is that it is very stable, and therefore particularly suitable for sending out in carboys to small sewage works where the quantity of effluent is small, and would not call for the installation of an electrolyser. The chlorides in the treated liquid are only very slightly increased by the use of this new form of the solution.

Section 2.—Application of Chlorine to Sewage.

My first series of experiments was made in 1904, and demonstrated the efficiency of chlorine so derived in acting as an oxidiser, deodoriser, and germicide on sewages and effluents. The publication of my results in the *Journal of the R. San. Institute* (vol. xxvi., No. 7, 1905) and elsewhere* was succeeded by the investigations on similar lines of Phelps and Carpenter on the sterilisation of sewage filter effluents (U.S. *Technology Quarterly*, xix, 47, pp. 382–403, Dec., 1906), and of Kellerman, Pratt, and Kimberley for the Ohio State Board (U.S. Dept. of Agriculture, *Bull.*, 115, Oct., 1907). In these cases a solution of chloride of lime was used as being more locally available, but Phelps remarks that "the use of gaseous chlorine manufactured at the disposal works by electrolytic methods would, in the case of larger works, considerably reduce the cost. The process as thus outlined is entirely feasible, and in the case of large works it is cheaper than sand filtration."

Kellermann, Pratt, and Kimberley found similar results when working with calcium hypochlorite on sewages in America, and came to the conclusion that with a hypochlorite complete disinfection was effected in partially purified sewage at a lower cost than with copper sulphate. In their experiments they have determined the ratio of chlorine immediately absorbed and the oxygen consumed figure obtained by five minutes' *boiling* with acid permanganate, and find that there is no relation between these two figures. They confirm my 1904 work in showing that the chlorine consumption of sewage is influenced by the concentration of the chlorine, since when 10 parts per 100,000 of chlorine is added more than twice the amount of chlorine is absorbed as when 5 parts per 100,000 only are added; this points to the advantage, when using chlorine for sterilising, of adding it in small quantities gradually, in order that its sterilising power may not be interfered with or absorbed by the organic matter present.

The American writers have compared the ratio of the amount of hypochlorite used by the organic matter in the *cold* in five minutes with the amount of permanganate with five minutes' *boiling*, whereas in my experiments I have compared the amount of chlorine required for producing sterility, irrespective

* See also *Sanitary Record*, Oct. 6, 1904; Rideal, *Sewage and Bacterial Purification of Sewage*, 1906, p. 186.

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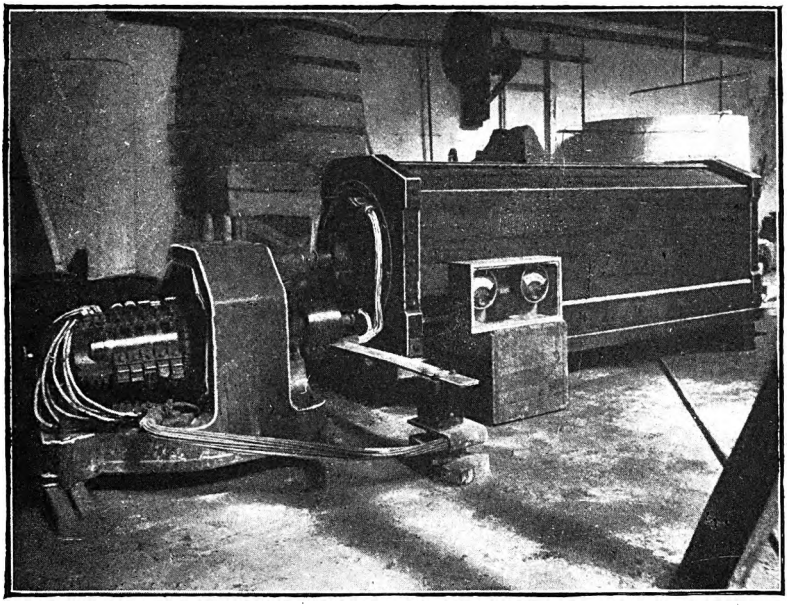

General View of "Oxychlorides" Electrolyser.

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of the organic matter present, with the amount destroyed by the permanganate in the *cold*. It is evident that the organic matter in different sewages in various stages of purification must be amenable in a varying extent to oxidising agents, but as it is in all cases a time reaction the essential point to observe in investigations of this character is not so much the quantity of chlorine absorbed by the organic and other reducing matters, as whether there is sufficient free or available chlorine present in the liquid for a length of time sufficient to cause necessary sterilisation. It is further obvious that, in ensuring sufficient available chlorine for sterilising work, some of the oxidising agent at the same time must be destroyed by the organic matter. This will be greater in strong sewages than in weak sewages, and will be greater in liquids in which the organic matter is in a condition to be amenable to chlorine oxidation. Sulphuretted hydrogen present in a sewage must influence very considerably the amount of chlorine required to be added, as it reacts immediately on free chlorine or hypochlorites. Nitrites, ammonia, and urea all form compounds with the av. Cl which have more or less sterilising effect. I found that the oxygen consumed from permanganate in five minutes in the cold as measuring the sulphuretted hydrogen and other easily oxidisable substances was a guide to the amount of chlorine likely to be quickly absorbed by the liquid, and in the earlier experiments found that when a maximum amount equal to 1·7 times this figure was used, the availability of the chlorine was sufficiently prolonged to ensure the desired sterilising effect. We have, however, frequently since obtained excellent results when the amount of chlorine was only equal to the amount of oxygen consumed from permanganate in five minutes in the cold.

In November, 1904, I was consulted in regard to a town sewage where complaints had been made of aerial nuisance, and oxychloride treatment was proposed as a remedy. The Council had already had experience with hypochlorites, and were then using permanganate, so that they were fully aware of the advantages of employing an oxidising agent for deodorising their sewage, They visited Guildford to examine the oxychloride process, and approved of it. The Local Government Board, however, suggested further experiments. and expressed a doubt as to whether subsequent bacterial purification might possibly be interfered with.

These points I had previously elucidated, as shown by the following instances from my earlier experiments :—

Experiment 59.—Rapidity with which oxychloride effects deodorisation. One part per 100,000 of av. Cl was added at the inlet of the branch pipe through which the septic effluent was passing at the rate of 1,000 gallons per hour. This pipe was 40 ft. long and 2½ in. bore. At the commencement a strong foul odour existed at the receiving chamber. The liquid was deodorised in passing through the pipe, and in less than an hour the whole tank had lost its odour.

Experiment 33.—A septic effluent giving a five minutes' oxygen figure of 3·41 parts per 100,000 was treated with 2 parts of av. Cl. This quantity reduced the five minutes' oxygen figure to 2·37 parts, was sufficient to deodorise the liquid, but not to destroy the organisms, therefore would not interfere with subsequent bacterial purification.

Other experiments made by Mr. Fieldhouse under my direction at Guildford in 1905 proved that oxychloride when used in small quantities sufficient to destroy foul odours, as from a septic effluent, at the same time acts as a powerful oxidiser, as seen in the five minutes' oxygen figure, and consequently must reduce the work required of the filters.

The Local Government Board, nevertheless, as is their usual practice with

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new work, were not satisfied without further prolonged experiments, and referred the matter to the Royal Commission on Sewage, whose experts recommended the construction of two exactly similar filters, one to receive oxychloride-treated septic liquor and the other untreated liquor. These were 9 ft. diameter, 6 ft. deep, and filled with broken coke of 1 to 3 in. size.

Second Series of Oxychloride Experiments. — The untreated liquor was conveyed from the main carrier of the Guildford Corporation septic tank to a small tank used as a constant head supply, thence to a second small tank furnished with a float to register the quantity flowing over two V notches, which led to two separate compartments containing syphons discharging periodically by sprinklers on to the beds. Oxychloride was stored in a vat connected with a constant level arrangement by which the solution was supplied in the amount required. The quantity of septic liquor passing on to the sprinkler filters was 50 gallons per cubic yard per 24 hours.

The maturing of the beds commenced on August 8th, and continued until November 22, 1906, when the Royal Commission's chemist, Mr. A. C. Carter, began to make investigations commencing with 25 per cent. of the five minutes' oxygen figure. It is necessary to know the five minutes' oxygen figure as in the Guildford experiments to get comparative results, by other methods factors must be introduced.

Guildford Method.—10 c.c. of sewage is placed in a bottle of about 250 c.c. capacity and 90 c.c. of tap water added, to which also is added 10 c.c. of 10 per cent. sulphuric acid and 25 c.c. permanganate of strength 0·0001 grms. *O* per c.c., using thio = 0·00008 grms. *O* per c.c., adding a crystal of potassium iodide after five minutes, doing a blank with 100 c.c. of tap water at the same time. This method gives a lower oxygen figure than by other methods, except direct titration by permanganate. Having obtained the oxygen consumed in five minutes in parts per 100,000, 25 per cent. of this figure was added of av. Cl; *e.g.*, if five minutes' oxygen figure = 2·0 parts per 100,000, 0·5 parts of av. Cl = 25 per cent. of that figure. Therefore, using oxychloride at 0·2 per cent. av. Cl, it requires 2·5 gallons of oxychloride to 1,000 gallons septic effluent or 5 gallons of a 0·1 per cent. solution. 0·1 per cent. solution was used during the earlier experiments as being more suitable for small flows, because of the gauging and the mixing. No. 1 bed received untreated sewage, No. 2 bed received treated sewage, and 25 per cent. treatment was carried out from November 22nd to December 6, 1906. Chemical analyses showed that oxidation by bacteria and other agencies had not in the least been interfered with, there being a slight improvement in the effluent from the treated sewage as compared with the untreated.

The five minutes' oxygen consumed figure and nitric nitrogen were as follows—

	Average of Last Week prior to Treatment.		Average of Last Week of 25 per cent. Treatment.	
	Five Mins.' Oxygen.	Nitric Nitrogen.	Five Mins.' Oxygen.	Nitric Nitrogen.
Untreated septic liquor	2·07	—	2·35	—
Treated septic liquor	—	—	2·3	—
No. 1 filter	0·51	2·20	0·64	1·87
No. 2 filter	0·50	2·02	0·58	2·0

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Therefore, prior to treatment the nitrates were higher in No. 1 filter, but at end of treatment No. 2 filter, which received the treated effluent, was slightly higher in nitrates. The av. Cl was sufficient to *nearly* eliminate aerial nuisance around the filter, and, in my opinion, would be sufficient for practical purposes, although sulphuretted hydrogen was not entirely destroyed when tested with lead papers fixed on the arms of the sprinkler. Four-fifths of the H_2S was removed (see *Report of Royal Commission on Sewage*, 1908, pp. 198–201).

On December 6th we raised the amount of av. Cl to 35 per cent. of the five minutes' oxygen figure, and with this amount it was agreed (1) that *complete* deodorisation was attained on No. 2 bed (all traces of H_2S being absent to lead papers placed on arms of sprinkler), and (2) that further oxidation had not been interfered with.

On December 10th it was decided to further increase the av. Cl. to 50 per cent. of the five minutes' oxygen figure, it being suggested that if a man carelessly put on an extra amount of oxychloride it might interfere with further purification. This augmentation was continued from December 11th to January 13th, and unexpectedly proved of decided advantage to the filter, there being an increase in oxidation, also a reduction of grey gelatinous growths; whilst the *B. coli*, which in No. 1 effluent were at least 50,000 per c.c., were less than 10,000 per c.c. in No. 2. The following figures show averages of the first and the last week of this treatment, and prove that even if a larger quantity of oxychloride is added than that required to deodorise, oxidation is not interfered with—

	First Week.		Last Week.	
	Five Mins.' Oxygen.	Nitric Nitrogen.	Five Mins.' Oxygen.	Nitric Nitrogen.
Untreated septic liquor ...	2·39	—	2·70	—
Treated septic liquor ...	2·29	—	2·55	—
No. 1 filter	0·78	1·10	0·55	3·0
No. 2 filter	0·80	1·07	0·52	3·53

The next point was to ascertain how much av. Cl would really be required to retard nitrification, and to this end the dose was increased to 100 per cent., four times the quantity that would be used in most cases for purposes of *deodorising*. This amount is sufficient to reduce coli from hundreds of thousands to less than 1 per c.c. when given necessary contact. This experimental plant was not designed for this purpose, so that av. Cl was passing on to the filters, dissolving up the growths and cleansing the media, which at first tended to produce an indifferent effluent; yet under these conditions the filter speedily recovered, and gradually surpassed No. 1 (receiving untreated liquor), as the following figures prove (January 14 to May 13, 1907)—

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	Early Part of Treatment.		Last Week in April.	
	Five Mins.' Oxygen.	Nitric Nitrogen.	Five Mins.' Oxygen.	Nitric Nitrogen.
Untreated septic liquor	2·56	—	3·85	—
Treated septic liquor	2·07	—	3·01	—
Effluent from No. 1 filter ...	0·94	1·06	1·22	3·39
Effluent from No. 2 filter ...	1·08	0·67	1·17	4·10

These results show how much No. 2 was behind and how quickly it has surpassed No. 1. The 100 per cent. addition broke up the growths that were on the surface of No. 2 bed, whilst No. 1 had a considerable growth which would either have to pass away as solids or else block up gradually the spaces betwixt the media. The pipes conveying the treated liquor were clean and free from growths, whilst those to No. 1 had to be repeatedly cleaned out to allow the syphons to work properly. Bacteriological tests showed coli to be reduced from 200,000 to *nil* per c.c. in the liquor, and that when No. 1 *effluent* contained 20,000 per c.c. No. 2 had only 2,000; and these came from the growths passing away as solids in suspension. Thus the 100 per cent. treatment surpassed expectations in that the filter improved even with such a large amount of av. Cl as was passing on to it. Consequently a still further increase to 200 per cent. of the five minutes' oxygen figure was tried from May 14th to May 30th, with the following average results for the last three tests—

	Five Mins.' Oxygen.	Four Hours' Oxygen.	Nitrogen.	
			As Nitrite.	As Nitrate.
Untreated septic liquor	3·40	10·16	—	—
Treated septic liquor	2·36	9·94	—	—
No. 1 effluent	0·80	3·49	0·09	4·85
No. 2 effluent	0·70	2·96	0·07	4·95

By the analyses, even with this excessive amount of av. Cl, the filter was only temporarily interfered with and finally was every bit as good as No. 1, receiving untreated liquor—slightly better if anything. *B. coli* were absent from 2 c.c. in the treated liquor, and spores of enteritidis were less than 10 per c.c. More coli and spores were passing away with the effluent, *B. coli* 2,000 per c.c., and enteritidis spores 20 per c.c. in No. 2, whilst from No. 1 the coli present in the effluent = 10,000 and enteritidis spores 200 per c.c. Here again the *B. coli* in effluent from No. 2 filter were apparently traceable to growths dissolved from the media and passing away as suspended solids.

Seeing that 200 per cent. did not stop the process of oxidation, it was decided to again increase the amount of av. Cl, and from May 31st to June 10th the amount added was 500 per cent. This now produced an appreciable difference in the amount of oxidised nitrogen in No. 2 effluent.

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The average of the analysis of the last three days' samples was—

	Five Mins.' Oxygen.		Four Hours' Oxygen.		Nitric Nitrogen.	Opacity.	
	Shaken.	Settled.	Shaken.	Settled.		Shaken.	Settled.
Untreated liquor	3·04	—	8·85	—	—	—	—
Treated liquor ...	1·18	—	7·78	—	—	—	—
No. 1 effluent ...	0·81	0·30	3·57	1·49	5·37	6″	over 12″
No. 2 effluent ...	0·87	0·59	3·94	2·45	3·64	5½″	over 12″

Bacteriological tests—

	Untreated.	Treated.	No. 1 Effluent.	No. 2 Effluent.
B. coli	500,000 per c.c.	Absent from 5 c.c.	5,000 per c.c.	Absent from 1 c.c.
Enteritidis spores	500 per c.c.	1 per c.c.	500 per c.c.	20 per c.c.

Av. Cl was absent from the effluent.

During the last week of treatment No. 2 filter showed distinct signs of recovery, nitrates rising from 2·90 to 3·75 parts per 100,000, and it was decided to increase the av. Cl to 1,000 per cent. of the five minutes' oxygen figure from June 11th, and as the septic tank effluent was very foul at times, the amount of av. Cl was often 50 parts per 100,000. This treatment was continued up to June 16th, and from June 27th to July 12th. On July 2nd av. Cl began to pass away with the effluent, and after this No. 2 filter went back rapidly, as seen by the figures below of special samples collected on July 11, 1907.

	Five Mins.' Oxygen.	Four Hours' Oxygen.	Nitrogen.	
			As Nitrite.	As Nitrate.
Untreated	4·88	11·84	—	—
No. 1	0·89	4·32	—	—
Paper-filtered	0·46	2·08	0·30	4·33
No. 2	1·42	8·64	—	—
Paper-filtered	1·40	6·88	*nil*	0·25

Bacteriological tests of the liquor passing on to No. 2 filter showed *B. coli* to be absent from 5 c.c. probably more, and enteritidis spores absent from 0·5 c.c., whilst in the effluent both coli and spores were absent from 2 c.c.

Recovery of No. 2 Filter after 1,000 per cent. Treatment.—To see how long No. 2 would take to become normal again, the filters were rested eleven days, when again untreated liquor was passed on to both. After three weeks No. 2

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surpassed No. 1 in oxidised nitrogen, as on August 12th it contained 3·82 parts, as against 3·51 parts in No. 1. This difference was maintained up to the time of dismantling the filters (for a fresh series of experiments) on August 29, 1907, when it was found that the filtering medium in No. 2 was considerably cleaner than that in No. 1.

These experiments from August, 1906, to August, 1907, were carried out by Mr. Fieldhouse under the superintendence of the Royal Commission on Sewage, who published an extract of the results in their Report of 1908, p. 200, and summarised their conclusions to the following effect—

1. That "35 per cent. to 50 per cent. treatment" with the hypochlorite solution is sufficient to do away with the offensive sulphuretted hydrogen smell of the Guildford septic tank liquor, leaving in its place a comparatively inoffensive odour of spent bleach and fresh sewage.
2. That the addition of this quantity of "oxychloride" in no way interferes with the efficiency of the filter. Indeed, it rather adds to it, by helping to keep down an excess of grey growths on the top of the filter.
3. That a very much larger quantity of oxychloride *may* be added, without any danger to the filter. In other words, there is a large margin of safety, so far as regards the accidental addition of too much oxychloride. Somewhere between "200 per cent. and 500 per cent. treatment" appears to be the limit of the quantity of oxychloride which can be added with safety.

A number of bacteriological examinations were made in connection with the experiments, and we ascertained that a dose of oxychloride, more than sufficient to remove sulphuretted hydrogen smell and kill *B. coli* in the liquid to be treated, may be used without prejudice to the purifying ability of a *mature* percolating filter.

The subsequent paragraph (281, p. 201) of the Report is somewhat surprising: "Our own experiments have shown that the offensive character of Dorking septic tank liquor can be destroyed by the addition to it of three grains of lime per gallon," as it is general experience that lime alone tends to rather increase than diminish nuisance.

Beyond the above conclusions, in my opinion the following are equally obvious—

(*a*) That sewage from hospitals or infirmaries may be freed from dangerous organisms by the use of oxychloride before passing on to sprinkler or contact beds, or land, or before entering into ordinary sewage systems, without in any way interfering with the usual methods of purification.

(*b*) That when beds are clogged up with growths internally or on the surface, these can be dissolved and washed through speedily, and that such beds quickly recover normal conditions. It is evident if growths are kept under control by at least occasional doses of oxychloride, that sludging up will be considerably delayed, and that the excessive quantities of solids which pass away—particularly when heavy growths are breaking up—will be avoided.

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THIRD SERIES OF OXYCHLORIDE EXPERIMENTS, 1907 AND 1908.

The next point was to ascertain whether a 25 to 35 per cent. treatment might be safely applied *during the maturing of a filter*, and how far it would retard or prevent growths and assist in the work of oxidation. It was also thought probable that oxychloride might enable fine media to be employed for sprinkler beds in cases where at present excessive growths prevent their adoption. On the other hand, we wished to determine whether oxychloride used in such quantities for deodorising on a continued and prolonged run might disturb the balance of organic life and effect some alteration in the results. For these objects the construction of the filters was slightly modified. The media were removed, and each filter divided into two compartments, having separate exits. Also galvanised iron channels were fixed 2′ 3″ and 4′ from the surface in each compartment for the purpose of collecting special samples.

The filters had one half filled with coarse medium as before (new coke from 1″ to 3″), the other half with new coke which had passed through a 1″ sieve and remained on a $\frac{3}{8}$″ square mesh, so that each sprinkler had now one-half rough and one-half fine medium 6′ in depth. The plant in other respects was the same as previously.

At the commencement, on September 12, 1907, the rate of flow was 50 gallons per cubic yard on each filter, No. 2 receiving the treated liquor as before, the amount of av. Cl for the first two weeks being 25 per cent. of the five minutes' oxygen figure. Afterwards the dose was increased to 35 per cent. of the five minutes' oxygen figure, and continued at this throughout the whole test. The first run was from September 12 to October 2, 1907 (11 days), when the Corporation shut down the septic tank (which had been in use 12 months) for cleaning. On the last day of this short run the average results were as follows (see also Curve IA)—

	Five Mins.' Oxygen.	Four Hours' Oxygen.	Nitrous Nitrogen.	Nitric Nitrogen.	Opacity.
Untreated liquor ...	2·40	7·74	—	—	—
Treated liquor ...	2·16	7·66	—	—	—
No. 1 rough	0·76	2·53	0·00	0·00	4″
No. 1 fine	1·24	2·60	0·90	0·51	$4\frac{3}{4}$″
No. 2 rough	0·60	2·45	0·20	0·34	4″
No. 2 fine	0·41	1·42	0·10	2·26	$5\frac{1}{4}$″

The above figures indicate a rapid rate in the maturing of filter No. 2, receiving the treated liquor; no growths had formed on either filter, and the material was clean.

The experiments were not recommenced until the tank had been filled 2 weeks to allow the liquor to become somewhat septicised, the beds resting for 15 weeks. On January 17, 1908, after the sprinklers had run for a short time, special samples were collected, and oxidised nitrogen was found to be absent from the effluents, so that the beds had to be matured again. The following were the progressive results of the dates mentioned. The beds were first worked intermittently for 6 or 12 hours a day, or on alternate days but on February 22nd 24 hours' continuous runnings were commenced.

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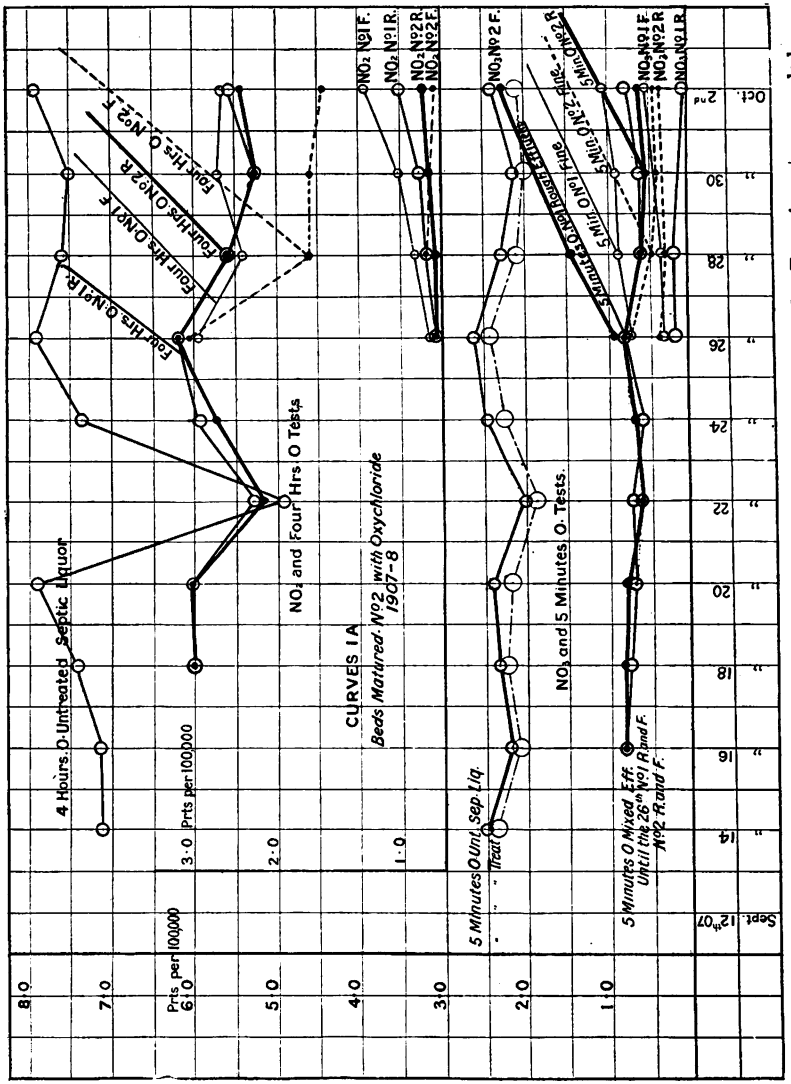

CURVE IA.—First run from Sept. 12 to Oct. 2, 1907. Beds not fully matured. Experiment suspended through the Corporation shutting the septic tank for cleansing.

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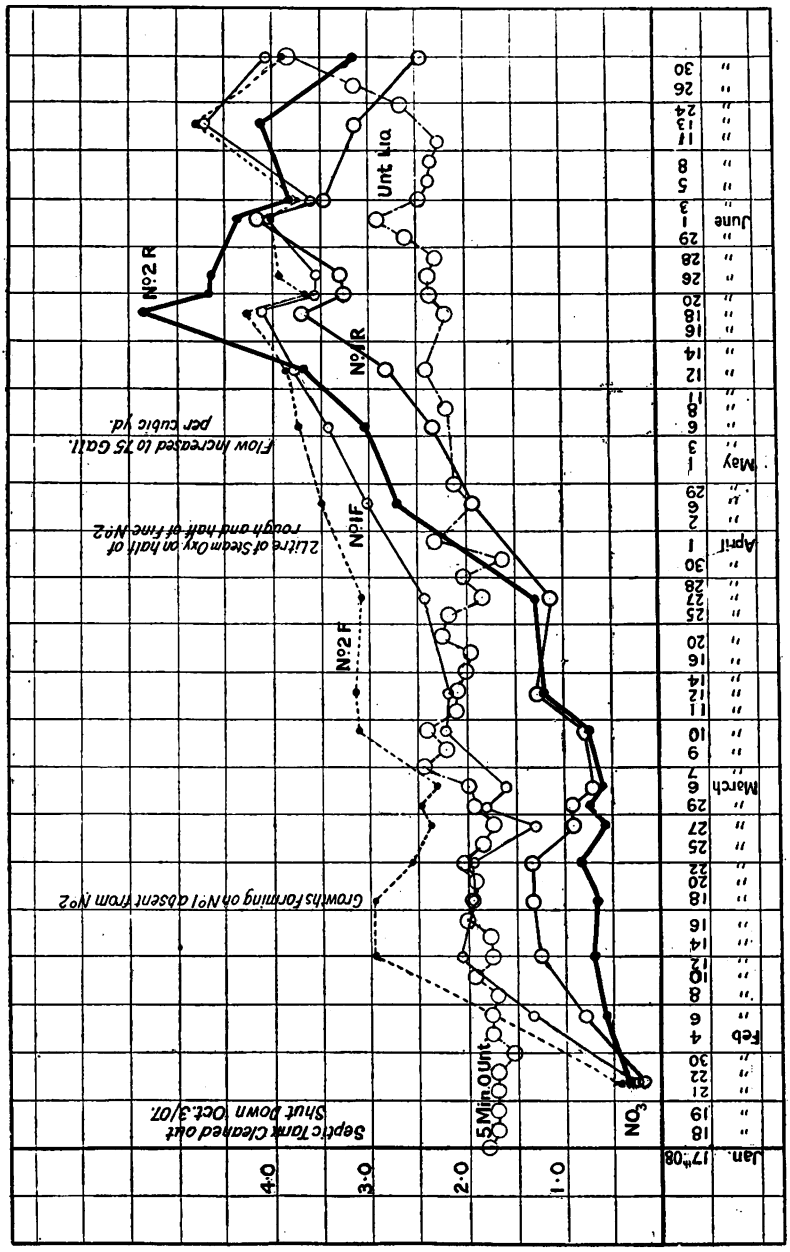

CURVE IIA.—Second run of sprinkler beds No. 1 and No. 2. Curve of nitric nitrogen (NO_3) on effluents. Also five minutes' oxygen consumed of untreated septic liquor. Following the cleaning out of septic tank and bed resting for thirteen weeks as described, pp. 187 and 190.

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	Oxygen Consumed.		Chlorides as Cl.	Nitrogen.		Opacity.
	Five Mins.	Four Hours.		Nitrous.	Nitric.	
Jan. 22nd						
Untreated liquid ...	1·60	8·20	8·90	—	—	—
Treated liquid ...	1·60	8·56	9·00	—	—	—
No. 1 rough ...	0·57	2·86	—	trace	0·19	4⅜″
No. 1 fine	0·44	1·36	—	,,	0·22	5¼″
No. 2 rough ...	0·73	4·08	—	,,	0·27	4¼″
No. 2 fine	0·47	2·48	—	,,	0·34	5″
Feb. 12th.						
Untreated liquid ...	1·68	8·96	—	—	—	—
Treated liquid ...	1·60	8·80	—	—	—	—
No. 1 rough ...	0·44	2·40	—	0·005	1·13	6¾″
No. 1 fine	0·40	2·08	—	0·010	2·02	8″
No. 2 rough ...	0·51	2·56	—	0·005	0·61	6½″
No. 2 fine	0·38	2·08	—	0·015	2·91	7¾″
Feb. 27th.						
Untreated liquid ...	1·68	8·00	9·5	—	—	—
Treated liquid ...	1·64	8·24	10·0	—	—	—
No. 1 rough ...	0·44	2·24	—	0·01	1·81	6½″
No. 1 fine	0·41	1·92	—	0·01	1·21	6⅝″
No. 2 rough ...	0·48	2·48	—	0·01	0·49	5¼″
No. 2 fine	0·35	1·44	—	0·02	2·31	8¾″
March 12th.						
Untreated liquid ...	2·04	8·64	—	—	—	—
Treated liquid ...	1·88	8·64	—	—	—	—
No. 1 rough ...	0·59	2·80	—	0·010	1·20	5¾″
No. 1 fine	0·46	2·24	—	0·020	2·11	5⅞″
No. 2 rough ...	0·62	3·04	—	0·005	1·17	5⅛″
No. 2 fine	0·44	2·08	—	0·030	3·11	6⅜″
April 6th.						
Untreated liquid ...	1·92	7·44	10·25	—	—	—
Treated liquid ...	1·92	7·30	11·00	—	—	—
No. 1 rough ...	1·44	1·90	—	0·02	1·89	10½″
No. 1 fine	0·35	1·40	—	0·02	3·00	over 12″
No. 2 rough ...	0·40	1·72	—	0·02	2·69	over 12″
No. 2 fine	0·38	1·17	—	0·02	3·49	over 12″

(For further particulars of analysis see Curve IIA.)

It will be seen that bed No. 2 is again maturing at a quicker rate, but the difference is not so marked as with the liquor from the septic tank before cleaning out. On February 19th growths were forming on No. 1 bed, but not on No. 2 ; on the 23rd and after the growths increased rapidly on No. 1, and there was only a slight formation on No. 2 bed. On March 5th the syphon of No. 1 began to choke, and the sprinkler refused to face the wind, owing to the slow discharge. The pipes and syphons were washed out with strong oxychloride, and the working went on properly. It was not until about eight months afterwards (November 18th) that in No. 2 cleansing became necessary on account of slowly accumulating growths ; they were cleaned out with strong oxychloride without disconnecting the pipes.

Samples of the media were examined on December 7, 1908, for sludge. No. 1, rough and fine, contained respectively 24·7 and 63·9 per cent. more deposit than No. 2 ; the latter was also visibly cleaner. The liquids from the washing of the media were tested by incubation ; of the *rough*, No. 1 developed H_2S, No. 2 a trace ; of the *fine*, No. 1 gave heavy H_2S, No. 2 none.

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TABLE Ia.

Special Samples at Various Depths.

Five Minutes' Oxygen Consumed Tests.

	Untreated Liq.	Treated Liq.	2′ 0″ Depth.				4′ 0″ Depth.				6′ 0″ Depth.			
			No. 1.		No. 2.		No. 1.		No. 2.		No. 1.		No. 2.	
			R.*	F.†	R.	F.	R.	F.	R.	F.	R.	F.	R.	F.
Oct. 3, 1907	2·20	2·12	0·94	1·00	1·00	0·81	0·68	0·75	0·68	0·62	0·62	0·75	0·65	0·43
Feb. 23, 1908	1·84	1·84	1·12	0·89	1·34	0·96	0·84	0·67	0·80	0·57	0·51	0·44	0·54	0·41
June 27, 1908	3·04	2·88	0·99	0·70	0·86	0·57	0·60	0·32	0·73	0·28	0·41	0·25	0·48	0·24
Sept. 21, 1908	3·03	2·77	0·89	0·74	1·07	0·64	0·53	0·32	0·54	0·32	0·39	0·28	0·46	0·25
Nov. 4, 1908	3·24	2·16	0·99‡	0·73	0·94	0·80	0·80	0·38	0·73	0·41	0·70	0·35	0·60	0·38
	—	—	0·70	0·57	0·80	0·67	0·48	0·28	0·60	0·41	0·41	0·25	0·41	0·32
Four Hours' Oxygen Consumed.														
Oct. 3, 1907	7·64	7·64	3·98	3·66	4·13	3·18	3·02	3·18	3·18	2·38	2·72	2·70	2·70	2·06
Feb. 23, 1908	7·52	7·68	4·16	3·44	5·12	3·36	3·28	2·64	2·88	2·16	1·92	1·84	2·08	1·68
June 27, 1908	7·52	7·68	3·20	1·76	2·88	1·76	1·76	0·80	1·60	0·60	1·04	0·64	1·44	1·04
Sept. 21, 1908	7·36	7·20	3·56	2·08	3·68	2·24	1·60	0·96	1·60	1·12	1·12	0·80	1·28	0·96
Nov. 4, 1908	7·04	7·04	4·16‡	4·48	3·86	3·68	3·04	3·36	2·24	2·56	3·20	1·92	1·44	1·53
	—	—	2·72	2·08	2·80	2·96	0·96	0·96	1·14	1·20	1·28	0·96	1·28	1·12
Nitric Nitrogen.														
Oct. 3, 1907														
Feb. 23, 1908			0·17	0·41	0·24	0·43	0·65	1·21	0·31	1·76	0·86	1·51	0·57	2·11
June 27, 1908			0·17	2·56	0·53	2·46	2·17	4·35	3·37	4·89	3·44	4·80	4·23	4·80
Sept. 21, 1908			0·90	2·72	0·45	1·73	2·76	4·73	2·85	4·89	4·43	4·75	4·38	5·30
Nov. 4, 1908			1·21	2·16	1·30	2·90	4·55	4·91	4·69	5·58	5·59	5·99	5·76	5·97
Average			0·60	1·87	0·63	1·88	2·52	3·80	2·80	4·28	3·58	4·26	3·76	4·54

* R, Rough bed. † F, Fine. ‡ In these lines following the ‡ the samples were shaken up before analysis.

(See Nitric Nitrogen Curve IIIa.)

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A number of tests on effluents were made from the various depths; the 2′ 0″ rough in all cases would not keep sweet after 24 hours. The fine 2′ 0″ on several occasions remained sweet and cleared themselves on standing. (See Table IA, also Curve IIIA.)

The fine samples show a better result than the rough both in five minutes' oxygen and in nitration. At first sight it would appear that the 4′ 0″ depth gives very nearly the same average purification as the 6′ 0″, therefore that the depth of the filter could be reduced, but this is not the case during the winter months nor at times of special impurity; and in general the greater depth is required for safety, particularly with rough medium.

Conclusions from the third series of experiments—

1. That a bed can be successfully matured when using oxychloride in such quantities as are required for preventing aerial nuisance.
2. That a bed may be thus matured at a quicker rate, as is shown by Curve IA.
3. That this treatment renders possible the use of fine-grade filters, which are usually not available on account of clogging by growths.
4. That it also renders easy the clearing of pipes, sprinklers, and syphons blocked by growths, without disconnecting the system.
5. That any place adopting the treatment for aerial nuisance has the additional advantage of (1) the retarding and destruction of growths; (2) assistance in the work of oxidation; (3) the means at hand of a very active deodorising and disinfectant agent, which may be made use of for general purposes.

The fact that oxychloride is a clear liquid free from suspended solids favours the use of automatic appliances for its addition in regulated quantities, and for this purpose Mr. Fieldhouse has designed a patent automatic supply and recording valve used at Guildford, which has been found simple and reliable for adding any determined amount in proportion to the volume treated.

Section 3.—Additional Notes on Special Points.

Behaviour of Treated and Untreated Effluent as regards Dissolved Oxygen.—A septic effluent showing a five minutes' oxygen figure of 2·16 parts per 100,000 was treated with oxychloride containing 0·1 per cent. of av. Cl in the proportions of 35, 50, and 100 per cent. of the five minutes' oxygen figure.

The treated and untreated samples were all shaken up with air in the same way at the beginning, so as to saturate them with oxygen; they were then allowed to stand in closed vessels at the ordinary temperature. The dissolved oxygen determinations have the following figures—

	Cubic Centimetres of Dissolved Oxygen per Litre.		
	In Original Liquids at Beginning.	After Shaking for two Minutes with Air.	After Incubating for Six Hours.
Untreated	3·43	6·22	0·37
Treated, 35 per cent....	3·43	6·22	3·06
Treated, 50 per cent....	3·53	6·27	3·34
Treated, 100 per cent.	3·62	6·50	3·99

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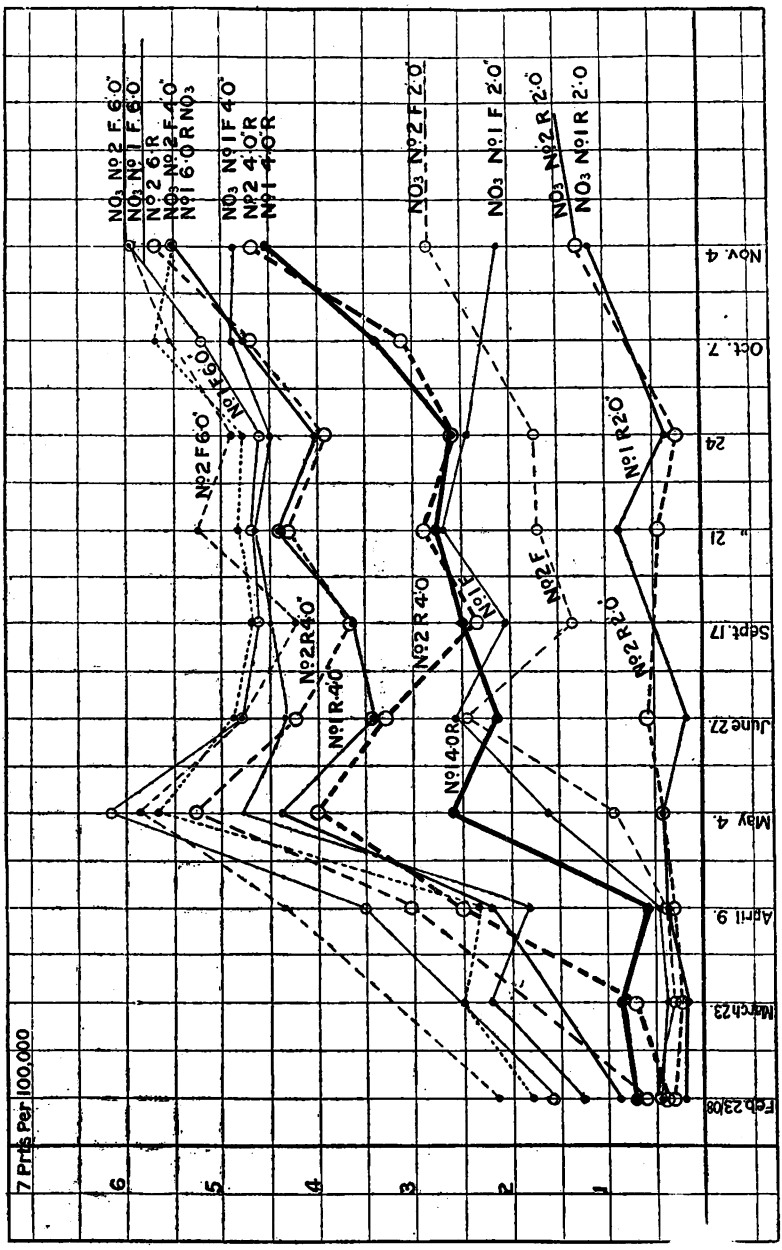

CURVE IIIA.—Special samples at various depths from No. 1 and No. 2 sprinkler beds. Nitric nitrogen curve (NO_3).

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These results prove that the treatment prevents the rapid de-aeration which septic effluents naturally undergo, and that the treated effluents maintain a satisfactory aeration.

The following are other examples—

Liquid Under Experiment.	Five Mins.' Oxygen.	Av. Cl. Added.	Dissolved Immediate.	Oxygen c.c. per Litre after 24 Hours.
I. Septic liquor	3·6	3·6	—	—
+ 75 % of fully aerated water	—	—	6·13	5·44
II. Septic liquor	2·24	2·24	—	—
+ 75 % of fully aerated water	—	—	6·73	6·13
+ 90 % ditto	—	—	7·15	7·10

This proves that the effluent would not cause any appreciable de-aeration if discharged into even a small body of water. The treated liquor takes up oxygen more rapidly than the untreated. Thus a sample which had received oxychloride equal to only 35 per cent. of the five minutes' oxygen figure showed when collected from the sprinkler arms 2·23 c.c. of dissolved oxygen per litre, while the untreated had only 1·30 c.c.

Besides being better in other respects, the effluent from a sprinkler bed that has received *treated* septic liquor also contains more dissolved oxygen than that from one receiving untreated liquor. The following are examples taken at a very unfavourable period, and also at a more favourable season—

	Cubic Centimetres of Dissolved Oxygen per Litre.					
	Dec. 12th.	Dec. 17th.	Dec. 19th.	April 6th.	April 7th.	April 19th.
Untreated	3·2	2·9	3·17	2·97	5·29	5·39
Treated 50 per cent.	4·6	3·8	3·30	—	—	—
Treated 100 per cent.	—	—	—	3·71	5·71	6·22

That a treated liquor will more quickly become fully aerated when agitated with air is clearly shown in the following instance on May 1st, where the relative difference is greater—

	In Untreated.	In Treated.
C.c. per litre of dissolved oxygen originally	0·74	2·23
Ditto after shaking with air for 1½ minutes	3·16	4·55
Percentage of full aeration acquired	about 50 per cent.	about 75 per cent.

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The fact that a septic liquor treated with oxychloride for sterilisation when added to a well-aerated river water does not deprive it of its dissolved oxygen, goes to prove that the treatment might be adopted without the expensive addition of the usual bacterial installation; as the presence of traces of av. Cl does not form a precipitate of solids, therefore it is particularly applicable in tidal and other large flowing rivers, or to shellfish or watercress beds.

Effect of the Presence of Available Chlorine upon the Dissolved Oxygen Test.—The dissolved oxygens were determined by Rideal and Stewart's modification of the Winkler process. This is not appreciably interfered with by the presence of available chlorine in the amounts occurring in the oxychloride treatment, as the following example proves.

A septic liquor was treated with 0·1 per cent. strength oxychloride, and after two hours' contact the available chlorine was 1·41 parts per 100,000, which is over the ordinary amount. Two bottles were filled, one having its available chlorine neutralised by arsenious acid; the other was untouched. The dissolved oxygen estimated at once was in the former 3·34 c.c. per litre, in the latter 3·53 c.c. If the av. Cl had yielded its equivalent of oxygen it would have added 0·32 part or over 2 c.c.

Disappearance of the av. Chlorine when mixed with Septic Liquors.—The sample of septic liquor showed a five minutes' oxygen figure of 5·28 parts per 100,000. It was treated in each case with the same proportion of av. Cl, namely, 6 parts per 100,000, or a little over 100 per cent. of the five minutes' oxygen. The solutions of oxychloride used were, however, of different strengths and characters, as below—

Strength of Oxychloride Solution used in per cents. of av. Cl.	Parts of av. Cl added per 100,000.	Time Required for the Disappearance of the av. Cl Reaction to KI and Starch.
New oxychloride, 0·169 per cent.	6	2¼ hours
New oxychloride, 0·084 per cent.	6	3 hours
Old oxychloride, 0·174 per cent.	6	15 minutes
Old oxychloride, 0·082 per cent.	6	1 hour 20 minutes
A sample of the same that had been stored a long time } 0·10 per cent.	6	1 hour 50 minutes

The words "old oxychloride" refer to a preparation made in the original manner; "new oxychloride" means the liquid obtained by the new process, in which certain additions improve the keeping properties; it will be seen that its available chlorine also has a more lasting action in contact with the septic liquor. Another important point proved is that in all cases the liquid should be added in a diluted rather than in a concentrated state; with a more dilute oxychloride when the same total amount of av. Cl is added, this av. Cl lasts longer, due to better mixing, and to its not being taken up so rapidly by the organic matter. This is shown by tables A, B, C.

It will be noticed in Table A 4·29 parts of av. Cl have been required, in Table B 2·2 parts, and in Table C 1·13 parts. The bacterial results show that the presence of traces of av. Cl has been in each case sufficient to remove

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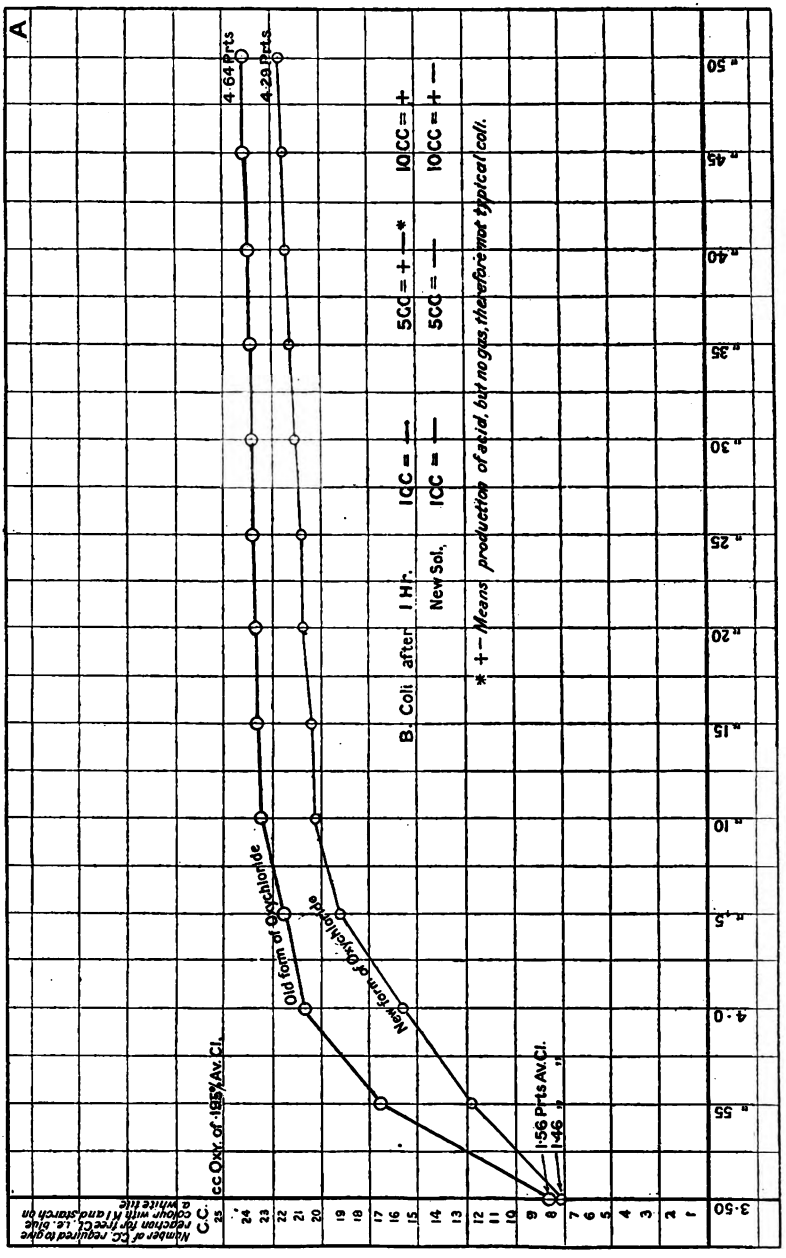
A
Number of CC required to give reaction for free C.L. blue colour with K I and starch on white tile
C.C.
cc Oxy. of 1·195% Av. Cl.
4·64 Pts
4·29 Pts
Old form of Oxychloride
New form of Oxychloride
B. Coli after 1 Hr.
New Sol.,
IOC = —
5OC = + —*
IOCC = +
5OC = —
IOCC = + —
* + — Means production of acid, but no gas, therefore not typical coli.
1·56 Pts Av. Cl.
1·46 " "

TABLE A.—Comparative rates of absorption of av. Cl with the old and with the new form of oxychloride solution. The test was carried out by adding to *one litre* of the septic effluent (with a five minutes' oxygen consumed of 4·56 parts per 100,000) measured quantities of the two solutions of 0·195 per cent. strength av. Cl at intervals as below.

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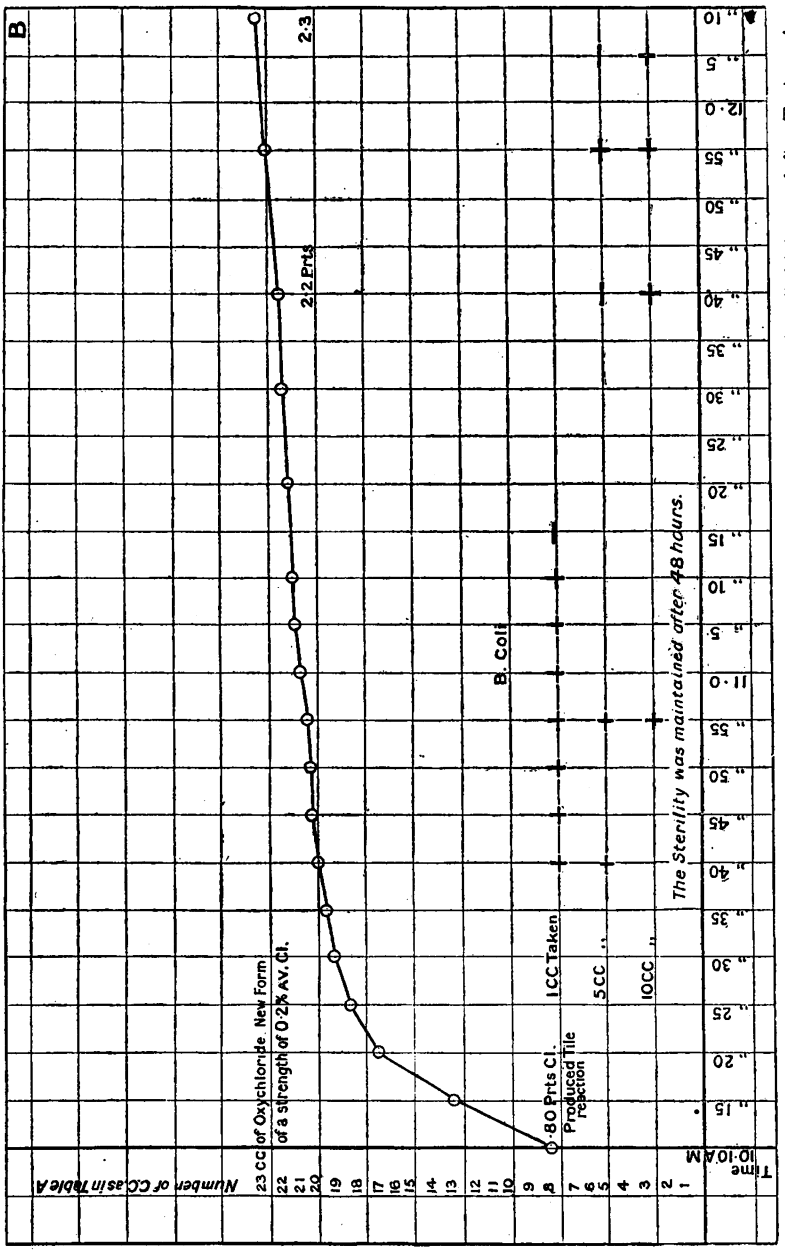

TABLE B.—Absorption of av. Cl when added progressively, and destruction of *B. coli* by the slight traces left. Tests as in Table A with a septic effluent giving a five minutes' oxygen figure of 3·04 parts per 100,000, but the oxychloride was added to *two litres* of effluent.

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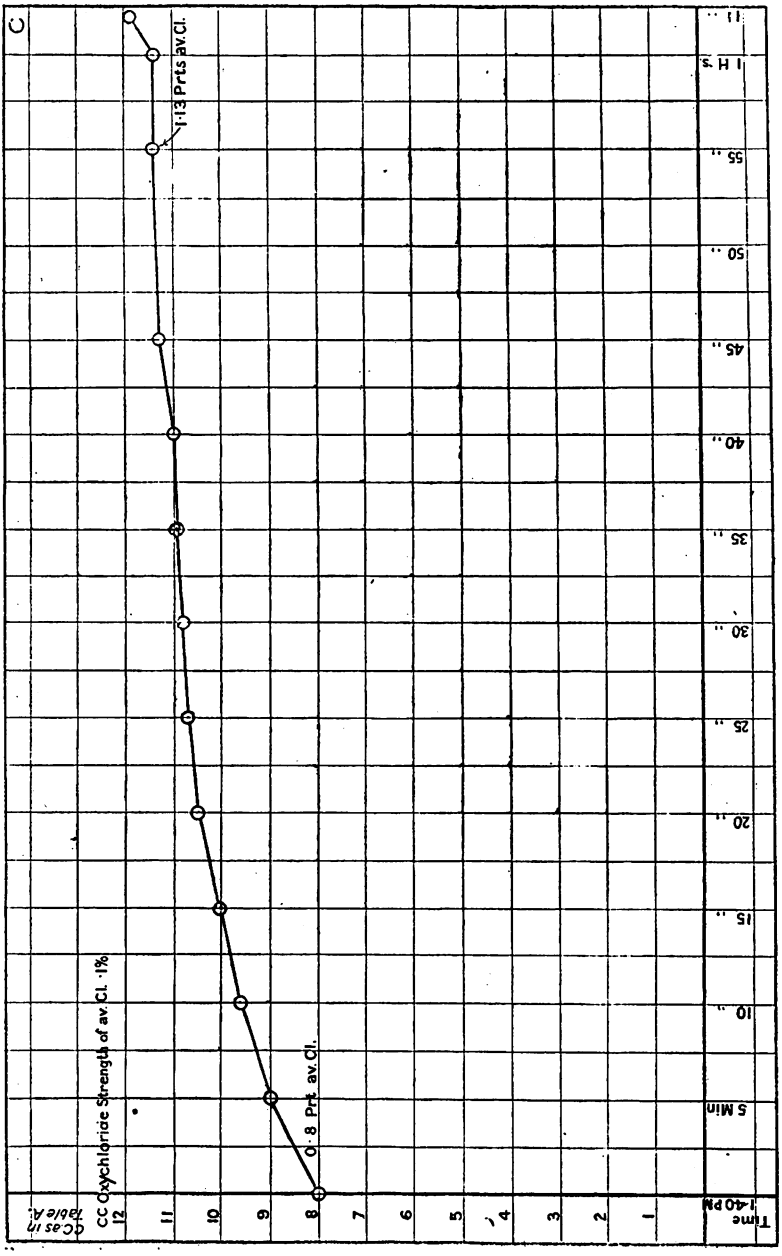

TABLE C.—Test as in Table B with solution of half the strength, namely 0·1 per cent. of av. Cl added to *one litre* of effluent.

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coli with one hour to two hours' contact. The percentages of av. Cl employed in relation to the five minutes' oxygen figure have been in A, with old form, 101·7, with new form, 94; in B, with new form, 72·3; in C, with ditto, 50·44.

In my former experiments with the "old oxychloride" I found that the best proportion to use on the average could be calculated by multiplying the five minutes' oxygen figure by 1·7, or as it is now phrased "170 per cent."

This ratio has now to be modified in the use of the new oxychloride for effluents, as the following experiment shows.

A tertiary effluent having a five minutes' oxygen figure of 0·366 was treated with an equal quantity, namely, 0·366 parts per 100,000, of Cl, or 100 per cent.; available chlorine was found to be present after *eighteen hours*, *B. coli* was absent from 10 c.c. after two hours' contact, and from 20 c.c. after three hours' contact. Hence an av. Cl equal to the five minutes' oxygen, or 100 per cent. treatment, in this case has been *more than sufficient*. Therefore it is not generally necessary to add more than this amount.

Aerial Nuisance.

(See *Royal Commission on Sewage Report*, 1908, pp. 195–201.)

Septic tank liquor possesses a stronger odour than raw sewage, owing to the breaking up of the organic matters in the tank and the formation of gases, and this liquor frequently gives rise to aerial nuisance when discharged by sprinklers on to percolation beds. The smell may be caused by a number of bodies, the more offensive of which are capable of deodorisation by oxychloride. The most prominent, especially when gas liquor enters the sewage, is sulphuretted hydrogen. The following table gives the amount of oxychloride required to be added to obviate the nuisance.

Strong septic liquor yielding a five minutes' oxygen figure of 5·2 parts per 100,000, and showing a considerable evolution of sulphuretted hydrogen by darkening a lead paper suspended over it, was tested with the lead paper after the addition of various proportions of oxychloride solution containing 0·2 per cent. of available chlorine. Results of two trials are given below—

Available Cl added in per cents. of the five minutes' Oxygen.	Sulphuretted Hydrogen evolved after Treatment.		Immediate Test by KI and Starch for available Cl left.	
Per cent.	I.	II.	I.	II.
10	strong	—	nil	—
20	distinct trace	—	nil	—
25	trace	distinct	nil	nil
35	nil	nil	nil	nil
40	—	nil	—	nil
50	nil	nil	nil	trace
75	nil	nil	trace	trace remaining after 5 minutes
90	nil	—	very distinct	—
100	nil	nil	distinct quantity remaining after 4 hours	very distinct

This shows that 25 per cent will be ordinarily sufficient to remove the odour, and that with such strong effluents 50 to 75 per cent. leaves a residue of av.

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Cl for further purification. In each case 35 per cent. has removed all the sulphuretted hydrogen. The oxychloride also prevents or retards the further development of sulphuretted hydrogen. Thus I found in comparing the effluents from sprinkler beds receiving treated and untreated septic liquors, that although both might at first be free from sulphuretted hydrogen, the latter developed it on incubation or keeping, while the treated usually did not, owing to the effect of the oxychloride on the organisms.

DISCUSSION.

Mr. W. Pollard Digby (*communicated*): The Society should be congratulated on having received from Dr. Rideal so excellent a Paper upon the bacteriological and chemical facts which have come to his notice in connection with the treatment of sewage at various stages and in various ways. The interest of the Paper to this Society is both electrochemical and bacteriological, and upon the bacteriological side a great deal is to be learnt from the Paper. On the electrochemical side, I would suggest that it is to be regretted that Dr. Rideal's clients have not placed in his hands data which can be of any relative value in the records of hypochlorite productions. For instance, we are told that a diaphragm is now being used by the Oxychloride Company. There will be no need to ask for the especial features of these diaphragms or matters which we regard more or less as works secrets; but, putting aside the question of diaphragm construction, we are told nothing of its utilisation. Some years ago, when the diaphragm process was first introduced for hypochlorite production, I had a great deal to do with the Crawford patent, in which cathode diaphragms were employed. I also experimented with anode diaphragms in the same way, of course, in which firms preparing alkali and bleaching powder by electrolytic process were then doing. In later hypochlorite productions I have found considerable advantage in the employment of double diaphragms, keeping the main body of the electrolyte from contact with either of the electrodes. I would ask, therefore, how the Oxychloride Company is using the diaphragm, and the further question—and a Society of this nature is entitled to ask, even if it does not receive an answer—as to what are the details of manufacture of the solution, and not merely what are the details of application. Now, in regard to manufacture, the information given upon page 179, while stating a current efficiency from which energy efficiencies can be calculated, does not state the strength of the solution at which this efficiency was obtained, neither does it give the salt consumption in, say, pounds of salt per pound of available chlorine produced. Therefore, when on page 180 we find recited a number of main advantages, it is surely legitimate to ask for some tangible proof of what those main advantages are.

Dealing next with the question of sewage treatment with available chlorine, this is a matter in which I take a great interest, as it is now rather more than eleven years since Dr. Rideal and I first met at Maidenhead, when Dr. Kanthack and Professor Robinson were investigating the hypochlorite then in use for such treatment. While I was then the paid servant of the owners of the patents, and while I had to look to Dr. Rideal and Professor Kanthack to tell me what the solutions were then doing, I can claim to be, with Dr. Rideal, one of the pioneers of sewage sterilisation. Dr. Rideal has, however, been the missionary pioneer, and his work later, at Guildford, has been of considerable value and very

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great interest. These results have been followed by the work in the United States of Phelps and Carpenter, and of Kellerman and others, who have only followed up Dr. Rideal's work, and have shown that sewage sterilisation can be cheaply effected.

When one considers that catchment areas are limited, and realises the cost of, say, a Welsh water scheme for London, it is surely obvious that great capital outlay can be saved if such an authority as the Metropolitan Water Board insisted on the sterilisation of sewage effluents entering the Thames. One does not claim, of course, that sewage sterilisation would entirely obviate the need for care and precaution at the water works, and it is possible that for treating drinking water we may have to consider not only available chlorine, but also the possibility of using ozone. But surely the time has now come when, speaking as electrochemists, and as practical scientific men, we should learn to call chlorine solutions by their proper chemical names. It is quite true that in times past I was associated with a Company which made hypochlorite solutions and sold them under a fancy name; but whatever name we give an electrolytical solution of hypochlorite of soda, whether we call it hermitine, electrozone, oxychloride, electrische-chlor, or electrische bleiche, it still smells as sweet as available chlorine, and still responds to the iodide test. Ought we not, therefore, to give up the fancy name except in regard to the apparatus used to produce the material, and give the liquid its proper name?—unless, of course, one of us is able to prove that his pet hypochlorite solution, with his favourite fancy name, will do more work with a gramme of available chlorine than anybody else's material with its fancy name. Some colour may be lent to this last point by reason of the fact that on page 195 a distinction is made between old oxychloride and new oxychloride, which merely serves to show that the same material may be well made or may be badly made, meaning by the latter unstable solutions which part with their available chlorine at too rapid a rate. We are all of us, who make hypochlorite solutions with a view to keeping them for some considerable time, in the habit of watching our temperatures, and also ensuring stability by means which we do not talk much about, except my friend Dr. Alexander, whose policy is that of frankness itself. In fact, I could wish that the Oxychloride Company were half as frank in regard to efficiencies and methods of working. While, however, my demands for information have been concerned with efficiencies, the information which has been supplied in regard to the application is of a most interesting character, and I must certainly confess my own surprise at the results obtained in which liquids have been treated before filtration in order to remove an aërial nuisance. Dr. Rideal is still the missionary pioneer in this field, but, in conclusion, I must say that I do not see any hope for a carboy trade to small sewage works where the quantity of effluent is small. Nearly every sewage works has motive power available in some form or another, and it is surely, therefore, the wisest policy to put down an electrolyser capable of immediate use, and so save the cost of freight of bulky liquids. Even taking a 15-gramme solution, one is paying for transport for a very large quantity of water and a certain amount of useless salt per unit of available chlorine, and in regard to which we should compare unfavourably with chemical manufacturers supplying chloride of lime, which is more compact, and gives a greater quantity of chlorine per unit of waste. The efficiency of the hypochlorite process of the future—and there seems to be room for several such processes—must surely lie in the isolated plant put down at the sewage works or

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water works, or, as Dr. Alexander has done at Poplar with such excellent results for his ratepayers, at some municipal depôt.

Mr. H. C. H. Shenton, after expressing his thanks to the Society and to the author of the Paper, said he was only qualified to speak on the practical side of the question, being an engineer and not a chemist.

He stated that after the reading of the Paper which he had written jointly with Mr. Pollard Digby, at the Society of Engineers in 1906, on the same subject, various persons had raised objections to the sterilisation of sewage at a Sessional Meeting of the Royal Sanitary Institute held at Stafford. It was then unhesitatingly stated that the proposal was altogether impracticable, and practically impossible. Many eminent authorities stated their grave dislike to the process, but only one definite argument was brought against the process of sterilisation, and that was that in times of storm a large quantity of sewage must necessarily pass into rivers untreated from storm overflows. He was glad to have the opportunity of demonstrating that this objection was by no means as serious as most people seemed to suppose. At the majority of works no storm-water was discharged from the sewers direct; it was conducted to the disposal works, and experience proved that a tank sufficient to hold one-quarter the dry-weather flow was sufficient, generally speaking, to intercept the sudden rushes of storm-water. People seemed to suppose because works had to be constructed to deal with a flow at the rate of several times the dry-weather flow, that this rate of flow was likely to continue unabated for 24 hours on end, and not only for 24 hours on end, but for 365 days in the year, and that provision must be made for sterilising, say, six times the dry-weather volume; this was obviously absurd. The Royal Commission Reports went to show that about one and a half times the dry-weather flow would include all storm-water throughout the year at places under normal conditions.

He wished to emphasise the fact that this quantity and much more besides could be sterilised quite easily. There remained to be considered the case of storm overflows from the sewers direct, which were inevitable, practically speaking, in some cases. If the case were sufficiently urgent, there was no engineering impossibility in conducting this water to the disposal works, but assuming it to be impossible to do so, there should not be the slightest difficulty in treating such overflow waters with the sterilising agent where they occurred. For instance, tanks of the sterilising liquid could be arranged at each point of overflow, and the liquid could be discharged in the usual manner by means of automatic valves; such overflows were only required on very large systems, where the cost of this extra attention would be of little consequence. The chief objections to sterilisation were due to extraordinary ignorance of the subject and to the impression that sterilisation by chlorine meant large masses of chloride of lime being discharged into the rivers. Although we were backward in this country, sterilisation of sewage effluents had been accomplished satisfactorily in America and in Germany. In the discussion on "Methods of Sewage Purification Abroad," a Paper read before the Boston Society of Engineers by Mr. H. W. Clark, Chemist of the Massachusetts Board of Health, it was pointed out that "during the past year we have, with the collaboration of Professor Phelps, carried out in Baltimore, at the Walbrook sewage testing station, a series of experiments on the disinfection of sprinkling filter effluents with solutions of commercial bleaching powder. Our results have been so extremely satisfactory that the final plans for the Sewage Disposal Works at Baltimore will include a chlorine disinfection plant." The United States Board of Agriculture published in 1907 results of most interesting experiments carried out at several places with large quantities of sewage effluent over an extended time, and

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gave annual costs of treatment per thousand gallons of effluent treated. Little had been done on a practical scale in this country, but signs were not wanting that English engineers were beginning to recognise the possibilities of sterilisation; for instance, the President of the Society of Engineers, Mr. Edward Silcock, in his inaugural address for the present session, gave it as his opinion that where sewage works send their effluents into rivers from which drinking water is drawn "it is probable that the future trend of public opinion will be in the direction of requiring the effluent from works so situated to be sterilised before being discharged into the river." Mr. Shenton also drew attention to the blame which attaches to the Local Government Board and the Metropolitan Water Board for acquiescing in years of delay between the sanctioning of a loan for sewage disposal works and the actual construction of such works, during which period the source of the water supply of London was polluted with unpurified sewage. Some blame must also attach to the commercial firms who took no trouble to bring before the public the appliances for sterilisation which had been shown to be necessary by the scientist, and which had been perfected in working by the engineer. They showed a discreditable lack of energy. Obviously sterilisation was necessary and economically possible; he had no doubt that it was coming, and he hoped that it would come in the near future.

Mr. Arthur J. Martin desired to associate himself with the previous speaker in acknowledging their indebtedness to the author for his lucid explanation of the subject dealt with. The preparation of the Paper must have involved an enormous amount of work, and it formed a valuable addition to our knowledge of sterilisation.

He took it that the actual volume of the sterilising liquid was negligible in comparison with that of the sewage.

He thought Mr. Shenton was hardly correct in stating that sanitary engineers disliked the idea of sterilisation; but it seemed to him that Mr. Shenton had rather slurred over the question of the wet-weather flow. The volume reaching the outfall in time of storm might be twenty or even fifty times the dry-weather flow, and unless the whole of this were sterilised there was little use in sterilising the ordinary flow, and to do so would only give rise to a feeling of false security. The first rush of storm-water, moreover, was generally exceedingly foul, containing a large quantity of putrescible organic matter, so that the amount of available chlorine required per gallon would be greater than in the case of the effluent ordinarily dealt with. The size of the sterilising plant must therefore be based, not on the dry-weather flow, but on the maximum storm-flow. Another point, not less important, was that it must be ready, at any hour of the day or night, to cope on the instant with a greatly increased demand.

Reference had been made to the sterilising plants in Baltimore and other cities in the United States, but sterilisation in that country would as a rule be a much simpler matter than with us. When he was last at Baltimore the sewerage system had not been installed, or at all events was not complete, for the sewage, in a part of the city at least, was running down the sides of the streets; but he presumed that, as in most other cases in the United States, the sewers were laid out on the separate system, so the flow would not be subject to the enormous variations which occur in this country.

For the reasons given he did not consider that sterilisation was likely to be of any general utility, at all events in Great Britain. The author was on surer ground when he based the claims of "oxychlorides" on their efficacy in the prevention of nuisance. He was quite right in describing this as a dominating factor in the question of sewage disposal. The chief reason for

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purifying the sewage at all was generally to prevent a nuisance, and this consideration had to be most carefully kept in view in selecting the mode of treatment and the site for the works. If by the use of "oxychlorides" a certainty is afforded that the purification of the sewage can be carried on without risk of nuisance, it would often be possible to utilise a site conveniently situated near the town, whereas in the absence of such a safeguard it would be necessary to carry the sewage to a considerable distance, involving a long and costly outfall sewer, and in some cases the additional expense of pumping. The cost of the chlorine treatment might thus be saved many times over.

The benefit to be derived from this treatment in the prevention of clogging of filter-beds and the pipes which supply them, and the consequent interruptions in the treatment of the sewage, was also important, provided the cost of producing the "oxychloride" was not too great.

He therefore agreed that Dr. Rideal had done good service by reading his Paper.

Mr. N. J. Bluman, referring to Mr. Martin's statement that, owing to the sudden increase of "oxychloride" required when storm-water came down, a very large plant for the production of such "oxychloride" would be necessary, said that he could not see why this should be the case, inasmuch as the storm-water would not require anything like as great a proportion of oxychloride to purify it as that which was requisite for the ordinary dry-weather effluent.

Mr. A. B. Thomson : Replying to the written criticism of the Paper, I am surprised at some of the points raised by Mr. Digby, because the paper which has been read to-night deals with "application of electrolytic chlorine to sewage purification and deodorisation by the oxychloride process," and not with the apparatus by which the electrolytic chlorine is produced. True, the author of the Paper asked us to give him some information about the apparatus, and in supplying that we tried to avoid controversial matter such as cost per kilo of available chlorine. The price of power, salt, and labour varies within wide limits in different districts even in this country, and to accept any arbitrary figure for power, &c., would be misleading to users in districts in which the conditions are better or worse than the arbitrary figures on which costs might be based. On the other hand, the author gives the current employed, voltage, salt consumed, and current efficiency in available chlorine at end of a given time, and this enables an electrochemist, or electrical engineer familiar with the subject, to work out the product and apply it to any given factors of power, salt, &c., in different districts. Mr. Digby said that the figure of current efficiency in available chlorine was useless because the strength of solution was not given, but that statement is absurd because it is immaterial, so far as current efficiency is concerned, whether we produce 200 gallons of 1 per cent. solution, 40 gallons of 5 per cent., or 20 gallons of 10 per cent. in a given time, and under the same conditions, as the percentage of current efficiency will be the same in each case. The fact which Mr. Digby evidently fails to grasp is that we get as high a current efficiency in producing 10 per cent. or 15 per cent. as in producing 1 per cent. solution, and this is, of course, one of the merits of our improved apparatus.

Coming to the diaphragm, Mr. Digby pays us a well-merited compliment in so far that he clearly admits that we have made more progress in that direction than he has. He says he has tried anode diaphragms, cathode diaphragms, and double diaphragms, but apparently without success: else why ask us to explain the construction and application of our diaphragm?

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We succeed with a single diaphragm, but then simplicity of construction is a leading feature of our apparatus. In regard to the construction and application of the diaphragm, that is a matter which has cost us a great deal in money and time, and I am afraid we must keep it up our sleeve in the meantime.

Another point criticised is the suggestion to send carboys of strong "oxychloride" to small sewage works. I agree with Mr. Digby that the ideal arrangement is to have an electrolyser on the sewage works, but we know of many cases in which it is quite the best thing to have supplies of strong oxychloride sent to the works. Every case wants dealing with on its merits and there are exceptions to all rules, even to having electrolysers on the works. His suggestion to use chloride of lime at small sewage works is utterly at variance with experience.

Mr. J. Fieldhouse said, with reference to dealing with storm-waters raised by previous speakers, the usual dry-weather flow installation would receive some portion of the flushes; afterwards the storm-water tank or tanks would deal with the remainder. By the time they would begin to discharge the sewage would be much more dilute, and would continue to be more so until the storm abated. The storm-diluted sewage, after becoming more uniform and settled, would pass over the end of the tank, if rectangular or square, into a chamber having a rectangular notch or weir, in which chamber would be fixed the automatic recording valve which would be set according to the flow and strength of the sewage or storm-water passing away, estimated by the 5 min. oxygen absorbed, and would thus vary the amount according to the varying flow. The "oxychloride" producing plant would be designed to meet local requirements as the amount of storm, &c., water varies so much at different places.

Dr. H. Borns: I do not differ from the other speakers as to the excellence of Dr. Rideal's paper. Dr. Rideal said in his introduction, however, that he should perhaps have brought his paper before a sanitary engineering society rather than before the Faraday Society. As we are the Faraday Society we are entitled to ask some information on the apparatus, the cell, and the process. I agree with Mr. Pollard Digby, therefore. There is very little electrochemistry in the printed Paper, and there was absolutely none in Dr. Rideal's remarks. Mr. Thomson has been good enough to lecture us on our ignorance; they had given all the information an electrochemist would want for his calculations. There are no such data. I can quite understand that Mr. Thomson does not wish to describe the diaphragms. But I hope that Dr. Rideal will, in his reply, be able to add some information on electrochemical points. Why the particular name "oxychloride"?

Mr. Charles Weiss asked whether the organisms Dr. Rideal had referred to as converting the albumen into nitrates were the same nitrobacteria now so prominently brought before the agricultural world by Professor Bottomley.

If the Paper did not give much elecro-technical information, it was at any rate highly important and practical. There was a small sewage scheme in North Staffordshire he was interested in, where the fine filters referred to were to be used. He would now certainly recommend that in this case the "oxychloride" process be adopted in addition.

Mr. J. H. Johnston remarked that Dr. Rideal had only tried chlorine deodorisation on the effluent from a septic tank as it was passing into the percolating bed. As many septic tanks were open and smell arose from the whole surface exposed, he would like to ask what method the author

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proposed for adding the oxychloride to the tank itself. When closed tanks were used, these were already ventilated, and by connecting up the surface of the percolating beds to the system of ventilation the addition of hypochlorite might become unnecessary.

Another important point in connection with the Paper was the evidence it contained as to the small part played by bacteria in the purification of sewage, the particular part of the process dealt with being the filtration of a tank effluent through a percolating filter. Members must have noticed how the author drew special attention many times to the fact that the addition of the chlorine very greatly reduced the numbers of the bacteria, and at the same time the treated filter effluent was much better than the untreated. Further, when estimating the sludge in each filter at the end of the experiments, he found very much more deposit in the untreated filter, where the bacteria might be presumed to have had every opportunity of acting, than in the treated filter. They could not, then, say that the purification in its essence was bacterial; and by the essence of the purification he meant, of course, the removal of the organic matter from the liquid. Recent research had shown that the purification was in reality a physico-chemical one, due to the fact that sewage was a colloidal solution. That point would be of special interest to members of that Society, because the famous chemist whose name that Society bore was one of the first to describe certain colloidal solutions. It would be travelling beyond the scope of the Paper to go farther into this question, but all sewage experiments as carefully conducted as those whose description they had listened to that evening could not fail to bear out that view.

Mr. F. E. Pollard: Dr. Rideal's work described in his Paper is unquestionably a valuable contribution to the subject dealt with; and in taking exception to the use of the term "oxychloride" as applied to the electrolytic hypochlorite solution, I desire only to express the opinion that the proprietors of the process have adopted an unfortunate and misleading name. The author's repeated use of the word "oxychloride" without quotation marks might lead those who are not chemists to suppose that oxychloride was actually contained in the liquid and gave up available chlorine. Of course, this is not the case; no oxychloride can evolve nascent chlorine as a hypochlorite does. The nomenclature of all chemical substances should accurately describe their constitution.

Dr. Rideal, in reply, agreed that the term "oxychloride" might be confused with such basic compounds as oxychloride of zinc, which contained no available chlorine. He was not, however, responsible for the name, and thought that the term "available chlorine" really represented all we knew about the constitution of the liquid which was useful for practical purposes. It probably contained ClO_2 ions as well as ClO ions; the former would give higher available chlorine than the latter. If kept cold, "ClO_3" ions (chlorate) were not present in the liquid, whether a diaphragm was used or not.

As to preventing aërial nuisance from open tanks, he thought that that difficulty seldom arose, as he had found almost invariably that the aërial nuisance only occurred when the liquid was disturbed. Bleaching powder solutions had been used regularly for many years for the sterilisation of the sewage at the Hamburg emigrant station as a safeguard from cholera, and at Hertford the sewage was similarly treated with "chlorides" before going into the River Lea, so that the additional cost of freight and transport was faced by these two authorities at the present time. The ease with which storm-water could be treated with automatic tanks had been referred to by Mr. Fieldhouse and Mr. Shenton.

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REVIEWS OF BOOKS.

The Theory of Valency. J. NEWTON FRIEND, Ph.D., M.Sc. Text-books of Physical Chemistry, edited by Sir WILLIAM RAMSAY. (London, 1909: Longmans, Green & Co., 39, Paternoster Row, E.C. Pp. 180. Price 5s.)

In this work the author presents us with a compact summary of the various theories of valency and structure from the days of Berzelius' and Davy's theories down to the present time. In some of the chapters the more important theories are considered in their general relationship to chemical facts, whilst in other chapters the author deals with the particular elements grouped according to the periodic classification. A special chapter is devoted to the electrochemical theories. Although the author has produced an undoubtedly useful work, and has compressed a large amount of scattered knowledge and speculation into a relatively small space, one cannot help being somewhat disappointed with the result. There is too much of the ancient business of juggling with strokes on paper, and not nearly enough of that quantitative modern physical and electrochemistry which has done so much to bring the valency question within the sphere of exact science. Remsen's trivalent halogens, for example, are a continual source of comfort to the author, and so is tetravalent oxygen. Mercurous chloride is Hg — Cl = Cl — Hg, hydrofluoric acid is H — F = F — H, and so on. When dealing with water the author says: "If the molecules are double, the formula is clearly $H_2 = O = O = H_2$." One had thought the days of this sort of formula-juggling were over.

Attention must be drawn to a striking omission. There is no mention of the work of Baly and his collaborators, or of Kauffmann, and yet surely their work is most intimately connected with the subject of valency.

In the chapter on electrochemical theories a good account will be found of the "electronic" theory of valency. This is, perhaps, the most interesting part of the book, although highly speculative.

In conclusion, it may be said that the author has tried to do justice to many theories, and, if the result is not entirely satisfactory, this is perhaps due to the extent of ground covered in a book of small compass. In spite of this compression, the present work is the most exhaustive monograph on the subject of valency which exists, and so is eminently worthy of careful perusal by every chemist and physicist.

Über die Oxydation des Stickstoffes im gekühlten Hochspannungsbogen bei Minderdruck. By Dr. ADOLF KOENIG. (Halle, 1908: Wilhelm Knapp. Pp. 76. Price 3m.)

This little book of 76 pages is a record of the results obtained by the author when carrying out his dissertation for the degree of Doctor of Engineering. It commences with an Introduction, in which the various

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reasons for endeavouring to fix atmospheric nitrogen are set forth, also the different methods, direct and indirect, by which the plants absorb the nitrogen which they require for their nutriment. The various methods for fixing nitrogen from the air are then briefly described.

Part II. is theoretical, and in it the author discusses whether the oxidation of nitrogen in the electric arc is a thermal process, and there seems little doubt that this at any rate is the case.

Part III. describes the various experiments carried out by the author, and finally, Part IV. discusses the results. The author considers that with flame arcs the process is thermal, but with cooled electrodes the phenomenon is a purely electrical one.

The little work is interesting theoretically, and helps to elucidate the difficult problem of oxidation in atmospheric nitrogen.

Monographien über chemisch-technische Fabrikations-Methoden. Band X. **Synthetische und Isolierte Riechstoffe und Deren Darstellung.** By Dr. RUDOLF KNOLL. (Halle, 1908: Wilhelm Knapp. Pp. 133. Price 4.50m.)

This is an extremely valuable and interesting monograph, and will be of undoubted value to those engaged in the perfume and essential oil industry. It commences with a general Introduction dealing with the chemical properties of perfumes—the influence of the presence or absence of certain groups. For example, the addition of a certain group may cause an odourless substance to assume an intense perfume. Thus salicylic acid and anthranilic acid are odourless, but by the addition of a methoxyl group perfumes are obtained. Again, trinitrotoluene has no smell, but the addition of the butyl group gives the intense smell of artificial musk, and so on.

Methods of chemical analysis and investigation of artificial and other perfumes in order to detect whether an adulterant is present are described. An interesting description of the different apparatus employed in the distillation and rectification of the perfumes is also included.

The Special Part follows, and in this the chemical properties of the various perfumes are described, and in some cases the different methods of preparation. The descriptions of the preparations are, we are afraid, rather too vague to be of much practical use, but at the same time one obtains a good deal of really useful information.

We congratulate the author upon his work, which shows evidence of much care and careful research.

Monographien über chemisch-technische Fabrikations-Methoden. Vol. XIV. **Komprimierte und verflüssigte Gase.** By Dr. H. TEICHMANN. (Halle, 1908: Wilhelm Knapp. Pp. 122. Price 6.80m.)

One of the most important advances in chemical technology which has of recent years taken place is in connection with the compression and condensation of gases. It is not many years since the compression and ultimate liquefaction of air or oxygen gas was looked upon as a wonder, and the quantities of the liquid gas produced were extremely small.

But by improved methods, the overcoming of engineering difficulties, the use of compression and then expansion, and the condensation of one gas first, which is then used to cool one which is still more difficult to liquefy, at last all gases have been liquefied. Furthermore, with the gradual conquest of the

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most refractory gases, the absolute zero has become nearer and nearer to our actual ken.

The book before us deals with the liquefaction of gases on an industrial scale. The first part is devoted to the physical aspects of the problem. The second chapter is headed "Mechanical Part," and begins with a theoretical discussion of the underlying principles involved in the condensation of gases. The second part of this chapter is of, to the practical man, the greatest interest, as it deals technically with the actual compression. The various pumps for compressing the gases, the different methods of cooling, and so on, are mentioned in detail.

The rest of the book is devoted to descriptions of the condensation of various gases, such as sulphur dioxide, ammonia, chlorine, carbon dioxide, nitrous oxide—which it is interesting to note is chiefly manufactured in this country—hydrogen, oxygen. The last section deals with the cylinders and other apparatus for holding the condensed or compressed gases.

The book meets a want, and the author is much to be congratulated upon the manner in which he has carried out his task. These technical chemical monographs will be found almost indispensable to manufacturers when once they realise that they are on the market.

Monographien über chemisch-technische Fabrikations-Methoden. Band XII. **Das Erdöl seine Verarbeitung und Verwendung.** By Dr. RICHARD KISSLING. (Halle, 1908: Wilhelm Knapp. Pp. 154. Price 5.40m.)

This monograph, after a brief Introduction, gives a most interesting historical account of the different views which have been and are held as to the origin of the world's mineral oil. Some consider that it has been entirely produced by a process of distillation under pressure of substances of vegetable origin which have in the course of ages been buried beneath the earth's surface. In 1877 Mendelejeff propounded the theory that it was produced beneath the surface of the earth by the action of water-vapour upon metallic carbides, the carbides having been produced by the great internal heat of the globe. This view was also accepted by Berthelot and Moissan, who eagerly upheld it. Sabatier thinks that it is formed by the catalytic action of nickel, cobalt, and iron upon ethylene and hydrogen.

On the other hand, there are many who hold that the vast petroleum wealth of the world has been produced from animal sources, either of a lower or higher form of animal life. To discuss all these theories would be extremely interesting, but as our object is to review the book, we must ask those who desire to know more of the subject to consult it.

The next section deals with the geographical and geological distribution of petroleum. In this respect America is most favoured, and in 1905 produced 62·1 per cent. of the world's supply, Russia being next with 25·69 per cent. It is of interest to note that in 1900 the positions were reversed, Russia leading with 51·49 per cent. and America producing 42·41 per cent.

The methods of drilling for the oil, with diagrams of the drills, are described, and Fig. 14 shows a good photograph of one of the great "gushers."

The main portion of the book is devoted to a careful description of the methods adopted for working up the crude oil and rendering it fit for the various uses to which it is put in commerce. This is decidedly a most useful monograph, and is written in a thoroughly practical style.

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Technical Methods of Chemical Analysis. Edited by Dr. G. LUNGE. English Edition edited by Dr. C. A. KEANE. (London, 1908: Gurney & Jackson, 10, Paternoster Row, E.C. 1 Vol. in 2 Parts. Pp. 1000. Price 52s. 6d. net.)

Lunge's German works are so well known that the knowledge of the publication of an English translation is sure to arouse widespread interest among British chemists. The difficulty in reviewing such a monumental work, however, is considerable, owing to the broad field which it covers.

Part I. contains 519 pages and has 146 diagrams of apparatus, all of which are drawn in line, and clearly show what they are intended to describe. The introductory chapter deals with methods of taking samples, laboratory operations, and comprises interesting considerations, which are non-chemical, of the arrangement of works' laboratories. Some of the apparatus here described is the same as that employed in the ordinary laboratory, but much of it is of a character which is not usually found outside of a technical laboratory.

The section commencing at p. 32 on Volumetric Analysis will be found of very great value; the calibration of the measuring instruments is first carefully gone into, and a calibration table is given on p. 37. The student of chemistry is often rather at sea as to which indicator it is best to employ under any particular case; the section dealing with indicators is worth a very careful study. Indicators are discussed both from the theoretical and practical side, and this naturally greatly enhances the value of the section.

Normal solutions are dealt with in the next section, commencing with the subject of standard acids. There has at one time and another been so much discussion as to the relative advantages of this or that substance as a standard or basis for acidimetry, that one is pleased to see that Lunge considers sodium carbonate to be the best; this has certainly always been the opinion of the reviewer. Following acidimetry and alkalimetry are the permanganate and other volumetric processes. Certain of the volumetric operations which deal with specific cases are only described when the necessity arises.

The next section deals with gas volumetric analysis, particularly in connection with nitrogen and carbon dioxide. A special section is devoted to Technical Gas Analysis. It is a pity that the apparatus of Bone and Wheeler is not described here, although a mention is made of it. This may, of course, be due to the fact of its comparatively recent publication. One might go through the volume in this way and point out all the excellent chapters and sections, but the space at our disposal will not permit of this.

Attention should, however, be directed to the exhaustive section on calorimetry and to the analysis of such products as hydrochloric and fuming sulphuric acid, the manufacture of sodium carbonate, caustic soda, and sodium carbonate, and the methods of analysis adopted technically.

Part II. This part deals almost entirely with technical problems, and commences with the methods of analysis of naturally occurring potassium salts. In the first place, the general methods for the determination are described and discussed. The platinum method is first described, and, considering the expense of the reagent, one is rather surprised to note that it is still considerably employed for the analysis of the potassium in connection with the Stassfurt deposits, although the perchlorate method appears to be coming more into vogue.

The next section deals with the analysis of cyanides and cyanogen compounds, and treats of practically all technically occurring cyanogen compounds—thus, for example, potassium cyanide, "spent oxide" from the gas works, potassium ferrocyanide, thiocyanates, &c.

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Other subjects are Clay, Aluminium Salts, Glass, Calcareous Cements, Hydraulic Cements, Drinking Water and Water Supplies, Sewage and Effluents, Soils, Air, and a variety of other analyses.

The book is not only a description of analytical processes which are employed in technology, but in many cases a description of the technical processes themselves is given. The best test of the value of a book such as this is to study and use it in the laboratory. This we have done, and have found it of the very greatest value. It is not, of course, meant for elementary students, because the descriptions of methods are hardly sufficiently didactic for such students. But no manufacturer can afford to be without it; no analytical chemist should consider his library complete without it, and all institutes where chemistry is taught should have it as a reference and stand-by.

The book is well edited, well got up, and the editor and his collaborators are to be heartily congratulated upon their very arduous work. We look forward with eager anticipation for Volumes ii. and iii., and trust it will not be long before they are ready.

Technical Chemists' Handbook. By Dr. G. LUNGE. (London, 1908: Gurney & Jackson, 10, Paternoster Row, E.C. Pp. 260. Price 10s. 6d. net.)

This very useful little book is not unknown in this country, as the first edition was published in 1884, under the title of "The Alkali-makers' Pocket Book."

The book is replete with valuable information and tables which are of use to both technical chemists and those engaged in general laboratories. The first part consists of General Tables, such as Density and Litre Weights of Gases and Vapours; Solubility of Salts; Specific Gravities of Solids; Freezing Mixtures; Volumes of Water at Different Temperatures; Specific Heats; Coinage of Different Countries, &c.

The special part is divided up into (1) Fuel and Furnaces, (2) Sulphuric Acid Manufacture, (3) Saltcake and Hydrochloric Acid, (4) Bleaching Powder and Chlorate of Potash Manufacture, (5) Soda Ash Manufacture by the Leblanc Process, (6) Manufacture of Soda by the Ammonia Soda Process, (7) Caustic Soda, (8) Electrolytic Alkaline Liquors, (9) Nitric Acid Manufacture, (10) Potassium Salts, (11) Ammonia Manufacture, (12) Manufacture of Coal Gas, (13) Calcium Carbide and Acetylene, (14) Examination of the Raw Materials and Products of the Manufacture of Fertilisers, (15) Alumina Preparations, (16) Cement Industry, (17) Preparation of Standard Solutions, (18) Rules for Sampling, (19) Comparison of the Hydrometer Degrees according to Baumé and Twaddell with Specific Gravities, (20) Value of Alkali per ton.

Each section has numerous useful tables and explanations in the text. This is a most valuable book to have in the laboratory, and after being used will become indispensable.

The publishers are also to be congratulated on the manner in which they have got it up—soft covers and rounded edges; the printing is clear and the paper good.

Electrometallurgy. By JOHN B. C. KERSHAW, F.I.C. (London: 1908. Archibald Constable & Co., Ltd., 10, Orange Street, W.C. Pp. 303. Price 6s. net.)

Electric Furnaces. The Production of Heat from Electrical Energy and The Construction of Electric Furnaces. By Professor WILHELM

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BORCHERS. Translated by HENRY G. SOLOMON, A.M.I.E.E. (London, 1908: Longmans, Green & Co., 39, Paternoster Row, E.C. Pp. 224. Price 7s. 6d. net.)

If the almost simultaneous publication of these two books is an indication of the growing interest which English engineers and metallurgists are now taking in the subject of electric furnaces, the nature of the books, and more especially that of Professor Borchers' volume, is likewise an indication that electrometallurgical processes have not, for the most part, yet emerged from the tentative and experimental stages through which all new applications of science are bound in the first instance to pass. Professor Borchers' compilation, which will be invaluable for purposes of reference and as an historical guide to the development of the leading electric furnace processes, is very largely built up of information obtained from patent specifications. This shows, firstly, that the "inventor" has not yet altogether made way for the "engineer"—if we may be permitted to draw such a distinction—and, secondly, that the processes and appliances employed are still so novel that manufacturers have not yet overcome the natural reluctance of the pioneer to publish really authentic, complete, and up-to-date information regarding the details of their methods of manufacture. So we must, perforce, in the meantime, remain content with information that is either not quite complete, or not quite up-to-date, or—that is gathered from the records of the Patent Offices.

Within these limitations imposed on the authors by the circumstances of their subject, they have produced very useful manuals, certainly to those desirous of obtaining a general knowledge of electrometallurgical progress. This, indeed, is what Mr. Kershaw aimed at, and he has succeeded in giving well-compressed and very readable accounts of the processes that have either once received practical trial upon an industrial scale or are now in actual commercial use, dealing particularly with aluminium, bullion refining, calcium carbide, carborundum, copper, iron and steel and ferro alloys, glass and quartz, graphite, lead, sodium, tin, nickel, zinc, calcium, and such electric furnace products as carbon bisulphide, carbon tetrachloride, phosphorus, &c. Most of the processes described will be found familiar to those who have kept in touch with recent electrometallurgical development; but then the book is intended for those who have not kept in touch, and wish to do so.

Professor Borchers' book is of the familiar pattern. An extraordinary number of processes and appliances are described, of which the majority are either of historic interest only, or else have never advanced, or can never advance, beyond the region of ink and paper, or at the best the laboratory. But even this somewhat negative method of imparting instruction would be valuable if the author, with his wide experience, had only deigned to criticise and select as well as describe. The unfortunate absence of such criticism and the necessary brevity of treatment in the case of the majority of the processes described, of course, greatly diminishes the value of the book as a text-book, or as a guide to students or practical workers, reducing it practically to that of a book of reference. The writer must confess that even he could not pluck up courage to read the book through, as reviewers usually do, of course. It is really a very great pity that Professor Borchers does not use more discrimination in his compilations, for the present volume contains a considerable amount of very interesting matter not easily obtainable elsewhere—at least, not in English; but it is likely to remain buried for ever from the eyes of the ordinary reader on account of the unattractive form in which this

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author persistently presents his wares. Professor Borchers, above all people, might have produced the really classical treatise on electric furnaces; unfortunately, we still await it.

Essays, Biographical and Chemical. By Sir WILLIAM RAMSAY, K.C.B., F.R.S. (London, 1908: Archibald Constable & Co., Ltd., 10, Orange Street, Leicester Square, W. Pp. 247. Price 7s. 6d. net.)

We welcome this very readable volume of essays; it is a species of literature that England is, perhaps, particularly lacking in. But having read them—and, we will hasten to add, thoroughly enjoyed them—the question remains, Is there an English public sufficiently educated in science to appreciate this type of literature? It is to be feared that even those that have appeared, for all the essays are reprints, in popular publications are often quite above the head of the average reader, while the professed scientist does not need his knowledge dished up in popular form. We may, of course, be wrong on both counts; it is to be hoped we are. In any case, Sir William Ramsay deserves a public when he writes in lighter vein on chemical topics.

The biographical essays deal with "The Early Days of Chemistry"—we were sorry to reach the end of this—Boyle, Cavendish, Davy, Graham, Black, Kelvin, and Berthelot, and they treat on their scientific work rather than on their not very exciting lives. Students, at least, should read and profit by these admirable sketches. The general essays deal principally with the "new" chemistry, the chemistry of radio-activity, atomic structure, and so forth. There is here some unavoidable overlapping, but they give between them a very adequate account of the present position of this side of physical chemistry. On somewhat different lines is the capital essay on the Aurora Borealis, with its interesting incidental discussion on the composition of the higher zones of the atmosphere; while the inevitable chapter on the value of science teaching, and especially of training in research, concealed from the unwary under the title of "The Functions of a University," brings this collection of excellent essays to a conclusion.

Lord Kelvin. An Account of his Scientific Life and Work (English Men of Science Series. Edited by J. REYNOLDS GREEN, Sc.D.). By Professor ANDREW GRAY, LL.D., F.R.S. (London, 1908: J. M. Dent & Co., 29 and 30, Bedford Street, W.C. Pp. 319. Price 2s. 6d. net.)

This is not a biography of Lord Kelvin in the ordinary sense, but is an account of his scientific work, expanded from a *Glasgow Herald* article, such as will make clear to the reader who has some acquaintance—some considerable acquaintance, in fact—with physical science the nature and range of his researches and discoveries. Great as the interest of the book will be to professed students of science, we doubt whether it will convey to the general reader, for whom presumably it is in some degree intended, a very clear conception of Lord Kelvin's mighty contributions to science, because it is written throughout in technical and often in mathematical language, and enters into detailed discussions which the man of ordinary education will certainly be unable to follow. Of course, there is ample room for a book of this kind, and it is needless to add that Professor Gray, who now occupies Lord Kelvin's chair in Glasgow, has done his work with thoroughness, accuracy, and perfect fairness; yet we cannot but think that there is still room for a more popular biography of Lord Kelvin, which will convey to the ordinary cultured public some idea of his tremendous achieve-

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ments. How tremendous those achievements were one can only properly appreciate when they are set down before us in order in a volume such as the present, when one is reminded simultaneously of the master's triumphs in practically every branch of physical science—dynamics, hydrodynamics, elasticity, heat, electricity, light, geology, cosmic physics, molecular physics. Was there ever a man before whose mind embraced so vast a range of natural knowledge, making discoveries of fundamental importance in every direction in which it moved?

The book contains three beautiful illustrations; a fine photogravure of Lord Kelvin as he appeared in recent years, a copy of a photograph taken in 1846, when he was twenty-two years of age, and a charming view of the inner court of the old college buildings at Glasgow, showing the Natural Philosophy rooms.

We cordially recommend this volume to all who care to take a serious interest in the subject, and, we may add, it is exceedingly good value for its small cost.

Gesättigte Salzlösungen von Standpunkt der Phasenlehre. By Dr. ERNST JÄNECKE. (Halle a. S., 1908: Wilhelm Knapp. Pp. x + 188, with 83 tables and 153 diagrams. Price 9m.)

The treatment of equilibrium problems from the standpoint of the phase-rule has become one of the commonplaces of present-day chemistry, and monographs on the subject have been written by Roozeboom, by Meyerhoffer, by Bancroft, and by Findlay. No new principles have been introduced, but the number of illustrative examples has in recent years been multiplied enormously and in the most diverse fields, alloys, minerals, salts, and organic compounds having been fully studied. The present volume differs from those which have been cited in that it is confined to a single branch of the subject—that of aqueous salt solutions. The wealth of detail that is provided will be realised from the inclusion of 153 diagrams, some of them illustrating general conditions, but the majority referring to equilibria that have been studied experimentally. The product, though scarcely suitable for a student's text-book, is a useful work for purposes of reference, and can be recommended to any who may wish to look up special cases or to find out the extent of the field that has now been investigated.

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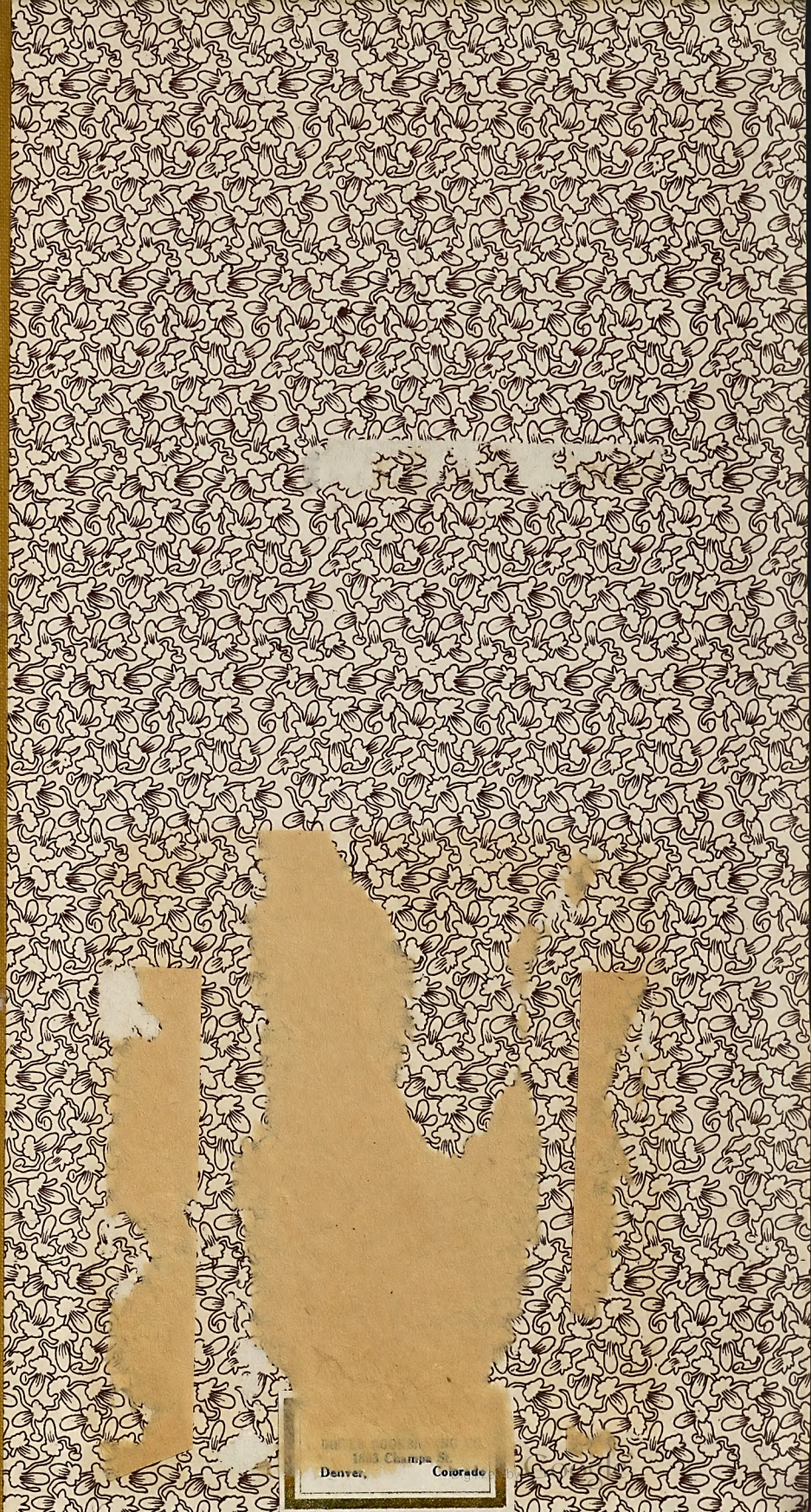
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